Chem Ed

EDITORIALLY SPEAKING

EDITOR'S NOTE. The internationally known demonstration school, The Little Red Schoolhouse (196 Bleecker St., N. Y. 12), is justly regarded as a pioneer in science instruction for "The Tricycle Age." The program has been the subject of articles in newspapers, the educational press, and of an editorial in C & E News (May 19, 1958). Dr. Randolph B. Smith, Director of the school, was asked to prepare a statement of the educational philosophy upon which the LRSH elementary school science instruction is based. The apt title of his remarks emphasizes that all readers of this page, regardless of the level at which their teaching occupies them, will find pertinence in what Dr. Smith has to say.

Science for the Millions

At the Little Red School House and its companion institution, The Elisabeth Irwin High School, we are eager, as are most schools, to discover ways of improving the quality of children's learning in science. Concerned not so much with more science but with better science, and more universal science, we are primarily interested at the outset to try to determine a few basic principles from which the problem should be attacked.

First and most obvious seems to us the necessity for beginning with a child's earliest years. The place where young scientists are born is in the nursery and early primary years. Sad the number of children's early science questions, often quite penetrating and profound, that fall on deaf ears—curiosities that are allowed to atrophy for want of a little patient nurturing. I am not suggesting that this requires formal courses in science in the nursery school any more than the first curiosities about sex demand full dress treatment from the birds and bees to Havelock Ellis and the Kinsey report. In both instances the answers need to be simple, honest, and just enough to leave the door wide open to further inquiry.

At the outset two things are important: first, a lot of painstaking listening to children with ears sensitive to the implications for science; second, much thoughtful analysis of children's science questions to determine the most promising approach for exploring them at different age levels.

But the gathering and winnowing of children's questions is not enough. How can one know enough to provide just enough answers, not too many, and just enough questions, not too few? This may sound a lot easier than it is. We suspect it may be one of the most profound jobs a science teacher can tackle, requiring not only that insight into science which makes possible translating great ideas into the true and simple but also a similar insight into children. We have little doubt that the investment of top professional talent of this kind in the early education of young children will pay rewarding dividends.

This prompts another of our perhaps rash generalizations as to principle. It is our impression that the essence of science is not fact but fiction! What we mean to suggest is that the essence of being a scientist, or a science teacher, is keeping alive the fascination with the unknown quite as much as gratifying the desire for the known. Whitehead has made the point most aptly when he says, "No man of science wants merely to know. He acquires knowledge to appease his passion for discovery. He does not discover in order to know, he knows in order to discover." And notice his emphasis on the word passion. In selecting the experiences for learning surely we must give as much weight to the aesthetic and emotional components as to the purely intellectual.

Finally there is the further principle that we are inclined to think is perhaps the most fundamental of all, namely that science is not a special domain or private preserve open only to those previously initiated in certain occult rites. Science belongs to everyone and is present everywhere. This is more subtle than appears at first glance. Science is not something separate from the rest of life. Science is only another way of looking at every aspect of life. Just as one may look at all dimensions of life from different perspectives, historical development or artistic design or philosophical meaning, so one may look at life from the point of scientific substance and function. It is simply a way of looking into things, around them and through them, a way of getting behind the obvious, of penetrating to the "heart of the matter" (we have such meaningful phrases if we take time to think about them).

The significant implication, at least for the early years, is that science is not something to be carried on primarily in a special place called a science laboratory or only by special people called scientists. One can probably safely say that any room at home or any classroom at school already has enough in it to serve as an adequate laboratory if everything in it were tracked to its lair. It may require various equipment for "looking into things and taking things to pieces"

but beyond that one can go a long way wondering, "What is it, what does it do, how does it do it, how did it get that way, what is it made of, what purpose does it serve, and what makes it tick?"—questions beyond number. And it will begin with the near at hand: the paper, the pencil, the ink, the crayon, the leaf, the flower, the turtle, the rabbit, until, increasingly, every ordinary item of life begins to become extraordinary.

In short, if we want children to be well-exposed to science and for science to become a universal fascination, it must be approached from a truly scientific point of view. There is an increasing number of good textbooks in elementary science to serve as source books for teachers but in our estimation, science cannot properly be taught out of a textbook. Science is not something to be sliced up into bite-sized doses to be retailed to children in well-packaged servings so much a day, nor should there be a stock diet for each given year. In the early years, science, to be real, has to be a derivative of all other aspects of the curriculum, flexibly developed and individually tailored to each group and classroom and drawing its stimulus and motivation from the daily substance of experience at home and school.

Approaching science this way, there is also the likelihood of another important educational derivative, namely the prospect that the scientist, even the highly specialized scientist, will not isolate himself in a world of his own separate from the artist, the musician, the novelist, the poet. It is important that each should have more than a nodding acquaintance with the other, that they should be able to converse together as intelligent laymen, should enjoy each other's work and see the creative effort of each as simply different facets of a multi-dimensional attempt to penetrate the inner mysteries of life. For the scientist to be content to dig himself deeper into his hole is as reckless as for the philosopher to stick to his ivory tower uncontaminated by the real world.

The habit of mind that steadily searches the obvious and near at hand for fuller meaning would appear to be the real essence of the scientific spirit. Here is where the appetite of the true scientist is first whetted, in finding the fascinating, the surprising, the unexpected close under one's own nose. In our judgment, this is not alone where the top flight nuclear physicists get their start—and the others working in the rarer atmospheres where major break throughs may be expected—but equally it is the breeding ground for the multitude of everyday scientists working on problems perhaps less world-shaking in their significance but none the less close to man's health and happiness. Whether the latter are the pressing problems of the under-developed nations of the earth or the science education problems of the local public school may be relatively inconsequential but we believe concerns of this kind derive from the approach to science education here outlined.

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A Chem Ed SYMPOSIUM

Radiochemistry in the Curriculum

Introduction

Within the past few years, it has become necessary to introduce radiochemistry and nuclear chemistry into an already crowded curriculum. Material has been developed at all levels from the general course to graduate work. This symposium was organized to share the experience of some of the leaders in the field in presenting this material at all of these levels.

The problem is essentially twofold: first, how to present radioactivity and nuclear chemistry in an interesting manner to the large numbers of undergraduate students, and, second, how to prepare our graduate students for research in this new field. There is general agreement that efforts must be continued in both these areas.

THIS JOURNAL has published many articles pertinent to this subject. Thirty-six of them have been reprinted in a volume distributed gratis by Nuclear-Chicago Corporation, Des Plaines, Illinois. This symposium[1] goes beyond that volume in covering all aspects of the subject.

The introductory paper, by Charles D. Coryell, of the Massachusetts Institute of Technology, included the historical development and an emphatic delineation of the importance of the subject. The abstract of his paper, entitled "The Radioactivation of Chemists," follows:

The history of the development of nuclear chemistry represents the commonest attribute of the field which is taught here and

[1] A symposium presented before the Division of Chemical Education at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

there in contemporaneous chemistry curricula. Its development was largely due to the interest and imagination of physicists, and its exploitation for chemistry was largely the result of the exhaustive demands on nuclear chemistry made by physicists and engineers in 1941–45 for the "atomic" bomb and required by nuclear engineers in the last decade for the development of military and civilian "atomic" power.

Let us define nuclear chemistry in broad terms as the chemical aspects of nuclear transformation, the separation and study of nuclear species (stable or radioactive), radioactive decay, the effects of radiation on materials, and the use of nuclides in chemical research. Such a definition is tantamount to saying nuclear chemistry is what nuclear chemists do. Nobel prizes in nuclear chemistry have been given about as often to physicists —e.g., E. Rutherford, M. S. Curie, F. W. Aston, F. and I. Joliot-Curie, E. M. McMillan—as to chemists—e.g., T. W. Richards, F. Soddy, H. C. Urey, G. C. de Hevesy, O. Hahn, and G. T. Seaborg. Most of the teaching of the subject is based on the work of these, and of the Nobelist geneticist H. J. Muller and the physicists A. H. Becquerel, P. Curie, J. Chadwick, E. Fermi, and E. O. Lawrence. It is probable that particle physics and physics techniques (many more Nobelists) will furnish only a nebulous background, although the proliferation of huge electronuclear machines in the Bev (10^9 ev) range brings operations closer to direct chemical importance, making a "chemistry of the nucleus."

The extension of the periodic system is central to chemical education. In the known span of elements from 0 (the neutron, 1934) to element 102 (1958), the last ten are accessible as a result of transmutation in nuclear reactors (piles or bombs). Classical nuclear chemistry proved the importance of radiochemistry for uranium and thorium and provided impetus and techniques for the study of the transitory elements: polonium, radon (emanation), francium, radium, actinium, and protactinium. Cyclotrons and reactors give working quantities of technetium, promethium, and astatine. Thus transmutation and radioactive decay are the key to 22 elements. But all the other 81 elements have radioactive isotopes useful for their analysis and for the study of their chemical properties. One synthetic element is being manufactured on the ton scale. The role of uranium-233, uranium-235, and plutonium-239 in the power industry today emphasizes the importance of nuclear chemistry in the modern curriculum.

The number of stable nuclear species is about 272, and the number of naturally occurring long-lived ones which have persisted since the creation of matter is about 12, three in the heavy element region carrying in steady state about 40 radioactive descendents. The number of man-made radionuclides is about 1100. All but a few of the elements have long-lived isotopes convenient for tracer studies. The work in physiology and medicine with tracers such as hydrogen-3, carbon-14, sodium-24, phosphorus-32, sulfur-35, and iodine-131 has already saved more human lives than the two wartime atomic bombs destroyed.

Isotope separations on the gram scale have been made for all elements with more than one natural representative, and separations on the kilogram or ton scale are made for some (hydrogen, lithium, boron, nitrogen, oxygen, and uranium). Another very large field is radiation chemistry, with its very important sister field, radiobiology. The importance of thermonuclear reactions brings in stellar chemistry as a dramatic new field, and the work of nuclear chemists with radiochemical dating opens new fields in geology and the chemistry of the formation of the sun, the planets, the meteorites, and the comets. The importance of nuclear chemistry for teaching today cannot be underestimated.

A. B. Garrett of Ohio State discussed his successful work with freshmen. Robert H. Maybury, the University of Redlands, showed how undergraduates can do tracer experiments with minimum equipment and expense. His views have already been published in THIS JOURNAL.[2]

More advanced work was described by K. S. Vorres of the State University of Iowa and L. L. Quill of Michigan State, while A. F. Scott treated the very successful program inaugurated by him at Reed College.

[2] MAYBURY, ROBERT, J. CHEM. EDUC., **36**, 133 (1959).

John E. Willard of the University of Wisconsin then told about the graduate work in the nuclear field at his institution. He intends to publish this in detail later. Meanwhile, an abstract is presented here.

The phrase "nuclear chemistry and radiochemistry," as commonly used, encompasses interests ranging from those of the nuclear physicist interested in the systematics of nuclear transmutation and decay to the organic chemist who wishes to trace a reaction step with the aid of radiocarbon labeling. So a "nuclear" or "radiochemist" may be either a physicist with a need for a few chemical techniques or a chemist who uses some of the physical properties of atoms. Courses which could appropriately be discussed under the title of this paper include nuclear theory, counting techniques, chemical methods for the separation of the fission products, isotopes effects, and study of reaction mechanisms with the aid of tracers. As no student can become an authority in all fields, such courses are valuable primarily for students planning to specialize in the areas concerned. No department can provide course work in every possible specialty. The most important training which graduate work can give a student is training in solving research-type problems as he meets them, a perspective on where to go for the information, techniques necessary for such solutions, and a self-confidence in his ability to come to correct solutions.

This paper describes a course designed to give students an intelligent perspective on the preparation, properties, and uses of radioactive materials and the properties of ionizing radiations. It has been given at the University of Wisconsin for 12 years with an average enrollment of 70 graduate students from ten academic departments. The mutual interests of the members of this varied group include the following: all may sometime want to employ radioactive tracers in their research; all need to be able to appraise critically literature reports of experiments using tracer techniques; all are scientists expected by their fellow citizens to be able to make an educated appraisal of newspaper reports on nuclear matters; and all are subject to radiation from fallout and the possibility of nuclear warfare.

The course is given by a physical chemist whose research is in the fields of chemical effects of nuclear transformations and radiation chemistry; it has visiting lecturers who are specialists in biochemical applications of tracers, medical applications of tracers, stable isotope tracers, and nuclear engineering. It follows no textbook but provides a 10-page bibliography of texts and references dealing with all types of nuclear applications. There is no laboratory work, but equipment is demonstrated in lectures, in tours to campus laboratories, and by discussion of descriptions of instruments in catalogues of commercial instrument companies. Sets of practice problems emphasize the use of fundamental principles and logical thinking to obtain answers needed in practical situations.

In addition to courses, any large graduate school has scores of graduate students employing radioactive tracers on thesis problems. Some examples of the value of such on-the-job experience are given. Comments are made on the value of the use of the facilities of the national laboratories for courses and as a supplement to university facilities for research.

The last paper in the symposium deals with S. T. Zenchelsky's successful course of a different nature at Rutgers.

It is evident that the fundamentals of nuclear chemistry and radioactivity should be and have been successfully integrated into the freshmen course, while additional material can be provided in later courses. More and more graduate students are being trained for research in an expanding field. Some of the most successful of the many pioneers share their experience in the papers of this symposium.

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Nuclear and Radiochemistry in the Curriculum in General Chemistry

Nuclear or radiochemistry is one of the most interesting, challenging, and integrating units of the first course in chemistry. Whereas the theory of combustion which usually is pointed to as the theory that marks the beginning of chemistry as a science, opened the field of understanding the chemical reaction processes and eventually led to the atomic theory, nuclear chemistry has made possible an understanding of a myriad of major processes or phenomena which for years were a great mystery to chemists. Among these are the relation of matter to energy, the transmutation of elements, the origin of elements, the energy-producing reactions of the universe, the structure of atoms, and the structure of the nucleus. These represent some major questions asked 25 years ago that are easily answered today in general chemistry. They thus deserve an important part of the curriculum of general chemistry today.

Let us illustrate how several of these become an important part of general chemistry course. Some of them may be interspersed; others may be taught as a unit.

$E = MC^2$. Here we have a relationship that has been a great mystery until recently. Nuclear processes offer direct evidence of the validity of this relationship. As we treat nuclear processes, this equation has become of commonplace utility, and the students of elementary chemistry and physics now make the calculation of the energy produced by either the fission or the fusion processes. Furthermore, this opens the door to another great mystery of nature—matter and energy are different but related manifestations of something in the universe—what that something is, is now the mystery.

The structure of atoms. It was the work of Rutherford (*1*) and Geiger and Marsden with atomic artillery obtained from radioactive processes only 50 years ago that gave us the concept of the nuclear atom. Geiger had said to Rutherford, "Isn't Marsden ready for a minor research problem?" Rutherford's reply went something like this: "Suppose we assign him the problem of studying the deflection of alpha particles when they are used to bombard thin metal foil and find out whether the alpha particles can be scattered through a large angle!" Marsden went to work on the problem and found that, whereas, most of the alpha particles penetrated the foil without deflection, some alpha particles were deflected through small angles, a few through large angles, and some alpha particles actually came backwards. Rutherford, in his interpretation of these data says, "It was then that I had the idea of an atom with a minute massive center carrying a charge." Rutherford goes on to say, "By considering how close to the nucleus the alpha particle could go, and yet be scattered normally, I could show that the size of the nucleus must be very small!" This was the birth of the concept of the nuclear atom (*2*).

The transmutation of elements. In more alpha particle bombardment experiments Rutherford performed the first transmutation experiment ever done in the laboratory. The reaction was:

$$_2He^4 + {}_7N^{14} \rightarrow {}_1H^1 + {}_8O^{17}$$

This is what the alchemists wanted to do for 1000 years. This was the beginning of hundreds of researches of this type and describes how man can not only change one element into another but also make new elements not found on the earth.

Artificial radioactivity. The Joliots, while studying alpha particle bombardment of light elements, found that a light metal target when bombarded with alpha particles becomes radioactive. Further studies of this sort have shown that essentially all the elements can be made radioactive by bombardment with neutrons or with high energy charged particles.

Presented as part of the Symposium on the Place of Nuclear and Radiochemistry in the Curriculum, sponsored by the Division of Chemical Education, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

Table 1. Reactions and Conditions in Various Regions of the Absolute Temperature Scale of the Universe

Element-forming region	5,000,000,000°		Collisions are so violent that complex nuclei are unstable; only stable particles are protons, electrons, and neutrons; exact temperature uncertain.
	50,000,000°		Nuclei fuse to form new elements; range of formation of the chemical elements; also energy-producing region.
	10,000,000°		Thermonuclear reactions begin.
↓ Atom systems being formed	1,000,000°		Translational energy very violent. Perhaps all atoms are stripped of electrons.
	6,000°		No molecules exist above this temperature; furthermore, atoms have lost one or more electrons; only ions and electrons exist.
↓ Molecules being formed	2,000°	Gas particles absorb energy	1. Translational motion 2. Vibration of atoms in molecule 3. Rotation of molecule 4. Electron transitions
	273°		
	0°		Vibrational motion of molecules in solid begins as energy is absorbed.

Energy-producing reactions of the universe. A study of nuclear reactions has given us a clear picture of the main energy-producing reactions of the universe. Principle among those in the reaction

$$4H^+ + 2e^- \rightarrow He + 2 \times 10^{10} \text{ kcal/g of mass converted to energy}$$

The energy produced by such nuclear processes is tremendous when compared to the relatively insignificant amounts produced by *chemical* processes, for example

$$2H_2 + O_2 \rightarrow 2H_2O + 136 \text{ kcal at } 25°C$$

Because of the packing-fraction factor (mass defect) the fusion reactions of nuclei, up to the mass of the iron group, are exothermic processes and hence can all contribute to the energy production process.

Another significance of these reactions, in addition to keeping the stars glowing, is that reactions such as these keep the temperatures high enough to make possible element-forming processes. This in turn leads us to an understanding of how the elements were formed or are being formed.

Reactions in sun and stars. As a result of the studies of nuclear reactions we can state now with confidence the reactions that are occurring at a given temperature in the most distant star. We know that at 10,000,000° the velocities of the protons are so high that they overcome the repulsive coulometric forces and come so close together that the attractive forces of the nucleus become effective and cause fusion reactions to occur. At higher temperatures higher charged particles are travelling rapidly enough to fuse together. Reactions of this type, together with neutron capture reactions, account for the formation of the chemical elements.

Origin of the elements. Men have wondered for centuries about the origin of the chemical elements. Prout, in 1815, proposed that they were made of hydrogen. Today, as the result of the work on nuclear reactions, we now know the processes by which the chemical elements of the earth were formed and are being formed in the sun and stars (*3*). There are some eight of these processes identified as the probable ones responsible for the formation of the elements but these can be described as two main processes: fusion reactions and neutron capture followed by decay. The other processes are modifications of these. (Table 2)

Nuclear structure. The only direct evidence we have of the structure of the nucleus comes from a study of the energy of radiations emitted from the nucleus in nuclear processes. Furthermore, in general the magnitude of the binding forces in the nucleus is obtained from similar data and nuclear masses.

Laboratory Experiments

There are numerous experiments that can be done in general chemistry. In general the choice should be determined by the principle to be taught or demonstrated, the safety features involved, and the availability of apparatus and materials. Let us describe three different types:

Collection of radioactive substances from the atmosphere. Much is being discussed today about fallout and radioactive contamination in the rocks, dust, water, and air around us, even the human body itself. This will probably be a growing problem in the years to come. It is possible to set up an inexpensive apparatus to measure fallout, and this is now being done in a number of laboratories. Anyone trying such a project will be

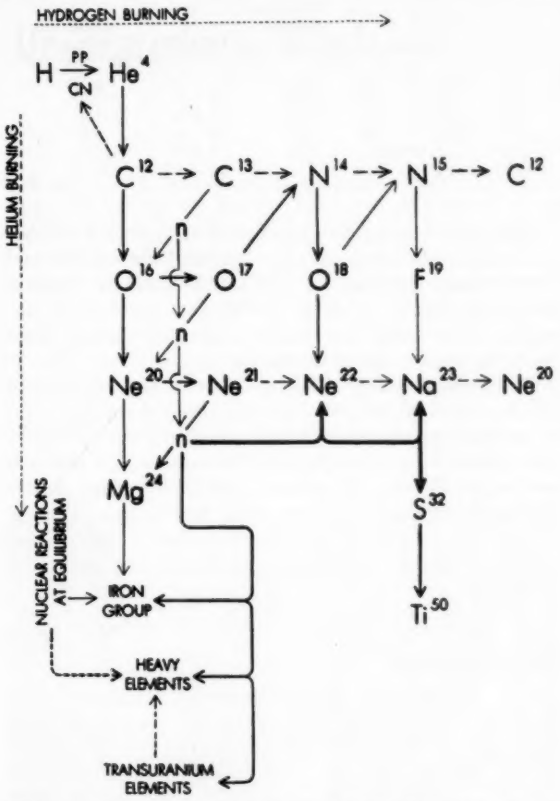

Table 2. Formation of the elements (simplification of the diagram given by Burbidge and Burbidge (3b)).

surprised with some of the results—an activity of about 30 minutes half life. This is due to adsorption on the filter of the solid products of the radon disintegration from the natural radioactivity of the earth. Here is a means of obtaining a radioisotope from the air, not from a cyclotron of the AEC. These products are mainly Pb-214, a beta-emitter of 27-minute half life, and Bi-214 a beta-emitter of 20-minute half life. The method of collecting a sample of these radioisotopes from the air is described by Diehl (*4*).

If one wishes to obtain other isotopes for half-life measurements, they can be obtained in safe, usable quantities from the Atomic Energy Centers. There is much literature available for instructions in the handling and use of radioisotopes. A very helpful manual available at the Atomic Energy Commission is entitled "Laboratory Experiments with Radioisotopes (*5*)."

Chemical analysis by neutron activation. One of the most sensitive methods of chemical analysis is the neutron activation technique. We have just completed a study on adapting this method to qualitative analysis for first-year college students. Neutron sources are readily available from Atomic Energy Centers. Using a 2-Curie neutron source of Be-Po in a large block of paraffin having a flux of about 10^6 neutrons per square

centimeter per second we have found the results shown in Table 3.

Table 3. Neutron Activation Experiments

Metal	Amount	Period of irradiation	Half life	Maximum cpm
As^{76}	315.2 mg	24 hr	27 hr	278
Au^{198}	262.5 mg	24 hr	2.7 d	588
Cu^{64}	500.0 mg	24 hr	12.9 hr	150
I^{128}	722.3 mg	2 hr	25 hr	543
Mn^{56}	1.0039 g	5 hr	2.6 hr	2561
In^{116}	127 mg	1 hr	54 min	2010

The experimental half lives were all within a few per cent of the literature values. Values between 200 and 2000 counts per minute are satisfactory for general chemistry work. This is a sufficient number of elements to use as an experiment in identification by half-life data after neutron activation.

Problems in isotope dilution. One of the very useful applications of tracers in analytical chemistry and in engineering makes use of isotope dilution techniques. The blood volume of a patient, the volume of a reaction system or of a storage system, and many other similar problems are solvable by this technique. This is simply an extension of the elementary calculation taught in the first titration experiment involving the equation

$$\text{Volume}_1 \times \text{normality}_1 = \text{Volume}_2 \times \text{normality}_2$$

but changed to

$$\text{Volume}_1 \times \text{activity}_1 = \text{Volume}_2 \times \text{activity}_2$$

This can make an excellent experiment in first year chemistry.

Literature

There is much usable literature available in nuclear chemistry. One of the very good reference texts is Friedlander and Kennedy, "Nuclear and Radiochemistry.(*6*)" An excellent laboratory manual is Bleuler and Goldsmith, "Experimental Nucleonics.(*7*)" There are others. Two good collections of papers in nuclear chemistry are the symposium papers in the JOURNAL OF CHEMICAL EDUCATION (*8*) and a bound collection of papers on nuclear chemistry from the JOURNAL OF CHEMICAL EDUCATION available from the Nuclear Chicago Corporation (*9*).

Conclusion

Nuclear or radiochemistry is one of the most interesting, challenging, and integrating units of the first-year course in chemistry. In theory it relates matter and energy; it gives an important means of determining mechanisms; it gives the answer to the alchemists' dream of making transmutations; it explains the origin of the elements and the energy-producing reactions of the universe. In the laboratory, for qualitative analysis, quantitative analysis, and general chemistry, it offers simple and intriguing experiments in neutron activation analysis, isotope dilution analysis, and tracer work. In presenting the method of scientific reasoning and the discovery process, the narration of how the discoveries in nuclear science "happened" to be made and how the high energy particles from nuclear processes were used to determine structure are some of the best illustrative materials and, too, are some of the world's great literature.

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(8) "The New Elements," JOURNAL OF CHEMICAL EDUCATION, Easton, Penna., **1959**.

(9) "A Collection of Papers from the JOURNAL OF CHEMICAL EDUCATION Related to Training and Experiments in Radioactivity," reproduced and bound by Nuclear-Chicago Corporation, 333 East Howard Avenue, Des Plaines, Illinois.

Nuclear Science Series—Monographs on Radiochemistry

A subcommittee on Radiochemistry under the Committee on Nuclear Science—National Academy of Science—National Research Council is publishing a series of monographs each dealing with the radiochemistry of a specific element. Each monograph, prepared by an expert, collects in one volume the pertinent radiochemical information and procedures required for work with that element. General and specific bibliographies are listed, physical constants are tabulated (including pertinent date for devising chemical analysis procedures) and the procedures found to be most useful are given in detail. The following volumes (Numbers NAS-NS 3001–3010) are available, the office of Technical Services, Department of Commerce, Washington 25, D. C.

3001 Cadmium, (James R. DeVoe), $0.75
3002 Arsenic, (Harold C. Beard), $0.50
3003 Francium, (Earl K. Hyde), $0.50
3004 Thorium, (Earl K. Hyde), $0.75
3005 Fluorine, Chlorine, Bromine and Iodine, (Jacob Kleinberg, G. A. Cowan), $0.50
3006 Americum and Curium, (R. A. Penneman, T. K Keenan), $0.75
3007 Chromium, (J. Pijck), $0.50
3008 Rhodium, (G. R. Choppin), $0.50
3009 Molybdenum, (E. M. Scadden, N. E. Ballou), $0.50
3010 Barium, Calcium and Strontium, (D. N. Sunderman, C. W. Townley), $1.25.

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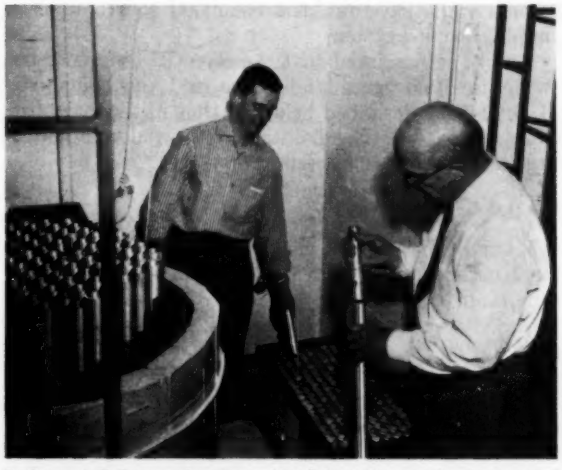
Radiochemistry— Advanced Undergraduate Work

Although Reed is a small liberal arts college, circumstances during the past 13 years have caused it to become unusually active in the field of nuclear chemistry, in training and research. These circumstances are of some interest and will be recounted briefly.

The start of the radiochemistry activity of Reed was a grant in 1947 from Research Corporation which enabled us to set up a small radiochemistry laboratory for use by four GI seniors in connection with their senior thesis projects. The next year the Division of Biology and Medicine of the Atomic Energy Commission invited us to participate in a new training and research program which they wanted to get under way. The purpose of the training program was to give young MD's the necessary background to enable them to employ radioactive materials in clinical work and in their research projects.[1] Also, in 1948, as part of the new AEC program, Reed received a major grant in support of two research projects involving the use of radioisotopes in the field of biochemistry. Two later developments which further improved our position were the acquisition in 1951 of an 84-curie cobalt-60 source and, in 1957, the construction of a subcritical reactor. Both of these will be described more fully below. During the past ten years our department has received further support from AEC in the form of grants for research in inorganic and physical chemistry.

Cobalt-60 source. In order to undertake a study of the chemical and biochemical effects of gamma rays, we obtained, in 1951, 84 curies of cobalt-60 in the form of metal rods. This, of course, is not a large source, as sources go today, but at that time it did represent a fairly sizable source of gamma radiation. We received this cobalt before the present strict regulations on handling such sources were put into effect. It came as bare cobalt metal which we had to encapsulate ourselves. Both we and our students, who were permitted to observe from a safe distance, learned something from the encapsulation operation.

Reactor. Our subcritical reactor was built by a senior, Harold Hammer, in 1957 (see photograph). This reactor is of the "pickle barrel" type and is similar to the original one built by Jordan at New York University in 1955. The reactor consists of a heavy wooden barrel (constructed by a local cooper) filled with water and containing, in a supporting rack, 2500 kg of natural uranium. The uranium, Hanford fuel rods, is on loan from A.E.C. Neutrons for the operation of this subcritical reactor are provided by 5 plutonium-beryllium neutron sources. These sources contain 80 g of plutonium and are also on loan from AEC. This reactor is used in several ways in the laboratory instruction. For example, in one experiment students map the neutron flux in the uranium-water lattice and also determine the ratio of slow to fast neutrons at different points. It is also not surprising that most visitors to the college, especially high school students, like to see the reactor and have it explained.



Professor A. F. Scott and senior student Robert Hammer loading natural uranium slugs into the "pickle barrel" subcritical reactor.

Undergraduate Course

This course has grown out of the need of our undergraduate students who anticipate using radiochemistry in their senior thesis projects. It started in 1948 as a seminar meeting one evening a week; it is currently a 3-hour course for one semester which includes three hours of laboratory work per week. The purpose of the course has always been to acquaint the students with the basic principles and techniques of radiochemistry.

It has been found convenient to use a text such as Friedlander and Kennedy's "Nuclear and Radiochemistry," although it is not possible to cover the book completely. It has been found advantageous to arrange the sequence of topics so as to enable the students to make the maximum use of the scheduled laboratory time. The laboratory work comprises the

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Presented as part of the Symposium on the Place of Radioactivity and Nuclear Chemistry in the Curriculum, sponsored by the Division of Chemical Education, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

[1] Sponsorship of this training program at Reed College was subsequently taken over by the Medical Branch of the Armed Forces Special Weapons Project (later DASA). The Reed course was the first step in a 12-month program for medical officers to acquaint them with the fundamentals of nuclear medicine. Many of the Armed Forces Medical Officers who have taken these courses have gone on to key positions in research and administration in their services.

usual experiments of an introductory course: (1) experiments with radiation detection instruments such as the Lauritsen electroscope, G-M tubes, scintillation detectors and, also, the usual types of monitoring instruments; (2) basic statistics of counting measurements; (3) tests of the fundamental properties of unstable nuclides and the characteristics of their radiations: radioactive decay, absorption and energy determination of beta particles and gamma rays; (4) assay of radioactive materials such as an unknown iodine-131 solution (simulated standard technique); (5) separations such as the extraction with water of Th-234 from an ether solution of uranyl nitrate and also a separation employing the ion-exchange procedure; (6) and finally, three activation experiments involving one or more of the Pu-Be sources, with a paraffin tub serving as the moderator. The first of these activation experiments is the activation of ordinary silver; the next is the preparation of I-128 by means of the Szilard-Chalmers technique; and the last experiment calls for the identification of an unknown element from the half life of the radioactive isotope produced by neutron activation. (7) The laboratory work of the course concludes with a special experiment by each student. Sometimes these involve studying effects of intense gamma radiation from the cobalt-60 source upon a simple chemical system.

It may be remarked that the essential difference between the undergraduate course and the course for M.D.'s, to be described below, is that in the former an effort is made to take advantage of the undergraduate's superior mathematical preparation.

Special Course for MD's

Many of the medical men who come to us for training in radiochemistry have been out of school for some time, and it is necessary, therefore, to start them off with review courses in mathematics, physics, and chemistry during the first two months of their six months' course.

Following this introductory session, these special students take courses in statistics, nuclear physics, radiochemistry, and the biochemical effects of ionizing radiations. The latter two courses are given by the authors.

Since the radiochemistry course is essentially the same as that offered to undergraduates, it will not be described further here. The course on the biochemical effects was designed primarily for the benefit of the physician students and will be described briefly below.

Biochemical effects of ionization radiations. In the course on the biochemical effects of ionizing radiations, consideration is given first to the ways by which energy from such radiations is deposited in simple systems such as air and water. Increasingly complex systems—inorganic salts in solution, organic substances, polymers—are then dealt with. Finally, the effects of radiations on living cells are discussed.

The laboratory work parallels the lecture topics. Using our large cobalt-60 source, the students irradiate various systems with gamma rays. Oxidation of ferrous ion in acidic solution[2] is used to determine quantitatively the amount of radiation from our cobalt-60 source. Other experiments range from the irradiation of a simple organic substance, sodium benzoate, and measurement of the phenolic substances produced, to the irradiation of mice and the determination of the efficacy of various known protective agents, e.g., cysteine, in preventing changes in the white cell count of the blood and decreasing the mortality rate. Simple, yet dramatic, is one demonstration of the effect of gamma radiations on seeds. Barley seeds irradiated for different lengths of time sprout and grow at rates inversely proportional to the radiation dose they have received.

[2] MILLER, N., *J. Chem. Phys.*, **18**, 79 (1950).

Undergraduate Research

Every senior at Reed College carries on a research project leading to a senior thesis on which he is examined orally at the end of his senior year. It is noteworthy that a student devotes about one-fourth of his senior year program to the thesis project and as a consequence some seniors are able to obtain significant and publishable results. It is in their senior thesis work that some of our students gain advanced experience in radiochemistry and radiobiochemistry.

Even during the first year (1947) of our radiochemistry program four seniors selected thesis topics in this field. One constructed and assembled apparatus for a G-M counting unit. Another, using ion exchange resins to concentrate inorganic ions, determined the radioactivity of water from the Columbia river. A third student, using mercury-203, estimated the rate of adsorption of mercury on silver surfaces in a highly evacuated system. Still another found in experiments with the silver coulometer that S-35 present in the electrolyte as sulfate is occluded in the deposited silver. A few of the senior thesis topics since that first year are as follows: one student used carbon-14 labeled methanol in water to estimate the occlusion of solvent in cathode silver deposited in the silver coulometer. Several students continued the study of the adsorption of mercury by silver and as a by-product of this work an attempt was made to prepare a radioactive daguerreotype. Another recent project has been the use of tritium in an investigation of the diffusion of cathodically-produced hydrogen through thin metal cathodes of palladium or steel. As an example of the special class experiments we may note here one which may be of interest to old-time chemists, viz., the use of strontium-90 and phosphorus-32 to estimate the occlusion of strontium ion and phosphate ion by silver chloride precipitated under the conditions of atomic weight determination.

Biochemical problems involving the use of radioactive materials have been selected by several seniors for their thesis work. Some have prepared compounds labeled with carbon-14 or with sulfur-35 and have used these in studying certain aspects of yeast and animal metabolism. In this work they have become experienced with radioautographic techniques and have dealt with the problem of counting weak beta emitting isotopes. Other students have taken as their problems the determination of the effects of gamma radiation on biochemical substances. One student found, for example, that when cysteine solutions are irradiated, significant amounts of alanine are produced in addi-

tion to the cystine and hydrogen sulfide which had previously been reported in the literature. Recently, one student became interested in activation analysis and, using a gamma spectrometer, studied the inorganic substances present in wood ash which had been irradiated in a reactor at Oak Ridge.

Conclusion

We can present a few general comments on our experience with radiochemistry training at Reed. First, many of the students who chose a senior thesis project involving radiochemistry or radiobiochemistry have continued in the same field or in one closely related to it in graduate school. A second observation is that the general student interest in the field of radiochemistry has apparently leveled off. This is partly due, no doubt, to the fact that many students have had their natural curiosity satisfied by discussions of radioactivity in their introductory physics and chemistry courses. The main reason, however, for the leveling off of students' interest is that radiochemistry is but one of many fields of chemistry which attract the attention of a young chemistry student today. At Reed we are hopeful of continuing a strong program in radiochemistry and in accordance with this hope we are including a special radiochemistry laboratory in the new addition to the chemistry building. This new laboratory will be ready for occupancy next fall.

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Teaching Radiochemistry at Rutgers

After World War II, in recognition of the new importance of nuclear energy, the School of Chemistry at Rutgers turned its attention to the problem of including such subjects as atomic and nuclear structure, radioactivity, nuclear reactions, etc., in the chemistry curriculum. The immediate effect was the expansion of the treatment already being given to radioactivity within the various undergraduate and graduate courses. Yet, except for a single laboratory experiment in instrumental analysis, a senior elective course, there was no means for providing the laboratory experience so essential to the comprehensive training of professional chemists. Moreover, it became abundantly clear that the lack of adequately-trained graduate students would serve as a limitation on the increased utilization of radioisotopes in thesis research.

This latter problem was also of great concern to several other university departments which had begun to use radioisotopes in research. Since financial limitations precluded the introduction of nuclear science courses into the individual curricula of the various departments, it was decided to organize an interdepartmental course, having an objective similar to that of the O.R.I.N.S. basic course.[1] It would provide training in the fundamentals of radioactivity theory and practice for persons within a variety of scientific disciplines. In this way, it would fulfill the immediate need of providing the necessary training for students intending to work with radioisotopes and, in addition, serve as a basis for the subsequent introduction of advanced, or more specialized, courses into the curricula of the various departments. The proposed course, under the sponsorship of the University Radioisotopes Committee, was to be designated: Science 491, Theory and Use of Radioisotopes.

Unable to obtain state funds for this purpose, the university turned to the chemical and pharmaceutical industry of New Jersey for financial support. The response was excellent; and, in 1954 there was established the "Radioisotope Center: for the exchange of information and furtherance of research," with an advisory committee consisting of members of the University Radioisotope Committee and industry representatives.[2] It was primarily as a result of the efforts of this committee that Science 491 was taught for the first time in the spring of 1955.

A sum of about $30,000 was thereby made available, the first year for instructional salaries and the purchase of laboratory equipment. An additional $6–8,000 was expended by the university for the conversion of existing laboratories. In the second year, 1956, an additional sum of $10,000 was furnished by the Radioisotope Center, with instructional salaries being defrayed by the university. In subsequent years, Science 491 has been carried by the university on its regular budget.

Course Content

From its inception, the course has been taught cooperatively by the departments of chemistry and physics. Its duration is one semester (15 weeks), consisting of two 75 minute lectures and one three-hour laboratory per week (4 credit-hours). Although Science

Presented as part of the Symposium on the Place of Radioactivity and Nuclear Chemistry in the Curriculum, sponsored by the Division of Chemical Education, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

[1] Overman, R. T., J. Chem. Educ., 28, 2 (1951).

[2] Members of the advisory committee were: J. B. Allison, Rutgers; R. R. Baldwin, General Foods; C. L. Brown, Standard Oil; F. G. Dunnington, Rutgers; J. Henderson, Johnson and Johnson; Y. E. Lebedeff, American Smelting; V. N. Morris, Johnson and Johnson; J. Potter, Rutgers; G. L. Royer, American Cyanamid; S. J. Toth, Rutgers; and P. A. van der Meulen, Rutgers.

491 is listed in the university catalogue as a senior and first-year graduate course, graduate students are given priority and hence predominate. The minimum prerequisites for admission are: (*a*) a major in science and (*b*) one year each, college algebra, general chemistry, and general physics.

In spite of the heterogeneity of preparation of the students, the course content is maintained at a fairly high level by assigning as much supplementary reading as is required in individual cases. Since no ideal textbook for this course is yet available, the reading assignments[3] are supplemented by extensive mimeographed notes as well as by references to the periodical literature and various government publications.[4]

About 45 per cent of the course content is devoted to nuclear physics and another 45 per cent to nuclear and radiochemistry. The remaining ten per cent is given over to health physics, isotope procurement, and laboratory design. The approximate number of class periods (75 minutes) devoted to each topic is shown in the following list:

Energy levels, atomic structure, radiation (2)
Nuclear stability, data and theory (2)
Characteristics of radiation and simple decay law (3)
Interaction of radiation with matter ($1^1/_2$)
Detection and measurement ($1^1/_2$)
Radioactive series and complex decay rates (1)
Statistics (1)
Nuclear reactions and fission, energetics (3)
Particle sources and accelerators (1)
Sample preparation and relative counting (1)
Activity standardization, absolute counting (1)
Tracer theory (1)
Concentration and isolation of radioisotopes (2)
Radiation and hot-atom chemistry (1)
Isotope exchange reactions (1)
Soft-beta counting methods (1)
Isotope dilution analysis (1)
Neutron activation analysis (1)
Laboratory design and isotope procurement (1)
Biological effects and health physics (3)

In addition, three films in the series, "The Radioisotope," are shown[5] outside of regular class hours, with attendance on the part of the students being optional.

Laboratory work is tied in closely with the lecture material. Experiments were largely taken from the literature with suitable modification.[6] Some were especially devised for this course. The experiments have been revised continuously so that they have reached a more-or-less stable form. Each is performed within one laboratory period of three hours.

The electroscope and G-M Counter, beta versus gamma efficiency
Beta absorption, range-energy determination
Gamma absorption, mass absorption coefficient
Scintillation spectrometry
Neutron activation, buildup and decay studies
Precipitation, evaporation, electrodeposition methods
Standardization of activity, absolute counting
Ion exchange separations
Coprecipitation and solvent extraction
Isotope exchange kinetics
Isotope dilution analysis
Health physics

Each laboratory section accommodates 16 students, working in pairs. Accordingly, there are available at least eight of each kind of apparatus, including electroscopes, G-M counters, scintillation detectors, sealed beta and gamma sources, and pocket dosimeters. Since only four differential pulse-height analyzers are available, the experiment on scintillation spectrometry is performed on different days by each half of the class. A detailed report on each experiment is required of every student.

The 25-millicurie Ra-Be source and paraffin moderator used for the neutron activation experiment is borrowed each semester from the physics department. Since it has only one sample irradiation well, there is a limitation placed on the number of students capable of using it within any one laboratory period. This situation will be remedied next year by means of a grant from the A.E.C. Office of Isotope Development which will make possible the purchase of a neutron source with three or four sample wells.

Two hourly examinations are given during the semester followed by a final examination (3 hours). These, together with the laboratory reports, serve as a basis for grading. Course credit is granted only to regularly-enrolled students who fulfill all of the requirements according to regular University standards. In order to satisfy the needs of those who are not registered for credit, e.g., faculty members, postdoctoral fellows, industry personnel, insofar as A.E.C. licensing is concerned, a certificate is awarded by the Nuclear Science Center to all who complete the entire course with a grade equivalent to C or better. Certificates were granted to about 70 per cent of those who completed the course.

The course here described has been received enthusiastically by students, who agree that it provides them adequately with the necessary foundation, in theory and practice, for the use of radioisotopes in research. There exists a feeling on the part of the author, however (which is borne out in his discussions with chemistry graduate students), that a number of the chemistry topics might well be omitted for the purpose of treating the remaining ones in greater depth, provided the course were intended exclusively for chemists. For example, such subjects as the various separation methods, with which chemists are already familiar, could be omitted in favor of a more detailed treatment of radiation chemistry. The laboratory experiments, on the other hand, do serve the chemists well in giving them the necessary manipulative experience as well as the experience of working with a variety (nine) of radioisotopes.

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[3] Texts in which the majority of reading assignments are made include: LAPP, R. E., AND ANDREWS, H. L., "Nuclear Radiation Physics," 2nd ed., Prentice-Hall, Inc., New York, 1954; FRIEDLANDER, G., AND KENNEDY, J. W., "Nuclear and Radiochemistry," John Wiley & Sons, Inc., New York, 1955.

[4] These include the various N.B.S. handbooks dealing with safe-handling of radioisotopes, monitoring, decontamination, and waste disposal, as well as selected A.E.C. reprints.

[5] These films are available on loan, free of charge. Procurement information may be obtained in the pamphlet: "Professional Level Film List, U.S.A.E.C. Film Library," obtainable from A.E.C. Technical Information Service Extension, Oak Ridge, Tennessee.

[6] The cooperation of Dr. Ralph T. Overman in supplying the details of some O.R.I.N.S. experiments was especially helpful.

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Neutron Activation Experiments in Radiochemistry

Neutron activation experiments provide a means of tying together a number of useful and important concepts in a radiochemistry course. These concepts are: (1) the half life of a radionuclide; (2) the absorption of neutrons by a sample using appropriate equations (see part II in the following calculation); (3) the concepts of partial and total cross section which indicate the probability for a particular reaction and absorption or scattering of neutrons. The particular reaction is usually radiative capture (capture of a neutron followed by emission of a gamma photon). The product nucleus is an isotope of the target nucleus with mass increased by one. (4) The rate of production of a given isotope in a neutron source can be calculated from the rate of absorption of neutrons, the partial cross section and relative abundances. (5) The total number of radioactive atoms of a given type is calculated from the rate of production, the time of irradiation and the rate of decay. (6) The relationship between the rate of decay and the fraction of the atoms that decay during a unit of time (the decay constant) and the number of radioactive atoms is illustrated in the calculation of the rate of decay of the sample. This can be made more practical by introducing the detection coefficient so that an expected activity can be calculated.

The Atomic Energy Commission has aided many schools in equipping radiochemistry laboratories for this purpose. However, many fundamental principles may be illustrated with a few relatively inexpensive items: paraffin-moderated Ra-Be neutron source, Geiger counter or scintillation detector, scaler and a set of absorbers. When more extensive equipment is available the experiments may be carried out with greater ease and speed.

Neutron Sources

Several types of neutron sources are available. The radium-beryllium type utilizing about 10 mg of radium is suitable for activating a few elements such as indium, manganese, dysprosium or gold to reasonable levels for simple laboratory experiments. This neutron source has a relatively high gamma intensity and a low flux (about 10^3 neutrons/cm^2-sec). A plutonium-beryllium source is preferable because it has no gamma emission. A one-curie source of this type provides flux of about 10^5 neutrons/cm^2-sec depending on the sample placement and is suitable for the irradiations listed in Table 3. The nuclear reaction in both of these sources is the emission of a neutron by the Be nucleus after alpha particle capture. Since most target nuclei have large cross sections (probability of capture) for neutrons of "thermal" energy, it is usually necessary to have the source and target in a moderator such as paraffin or water.

The irradiations here discussed were carried out in two reactors or assemblies to contain the source, moderator and sample. One was a model 9000 Nuclear Chicago water-moderated subcritical reactor utilizing five one-curie plutonium-beryllium sources. The other was a paraffin-moderated reactor made from the source shipping container and a single one-curie source. The Nuclear Chicago reactor is essentially a large stainless steel container filled with purified water and containing a large number of aluminum tubes spaced on a hexagonal gridwork. The center tube holds the Pu-Be neutron sources. The other tubes hold uranium slugs in capsules and are removable. The paraffin-moderated source is essentially a 15-gal. steel drum almost filled with paraffin. A center tube is used to hold one of the Pu-Be sources. Four other holes are drilled in the container to receive polystyrene tubes with either a cylindrical sample or flat sample. About $^1/_2$ inch of paraffin between the neutron source and sample holder is used as a compromise between the greater distance necessary to obtain completely thermal neutrons and the inverse square law reduction of flux as the sample is placed further from the source.

Figure 1 shows a cross section of the paraffin-moderated source set up for irradiation of flat samples. Cylindrical samples could be inserted in the tube in place of the flat ones. The geometry is similar for the Nuclear Chicago reactor.

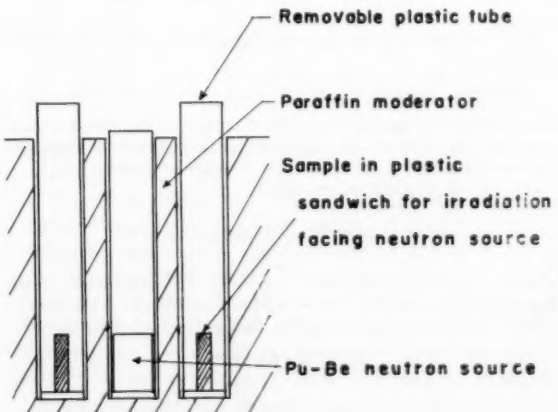

Figure 1. Paraffin-moderated neutron source.

Presented as part of the Symposium on the Place of Radioactivity and Nuclear Chemistry in the Curriculum, sponsored by the Division of Chemical Education, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

The one-curie Pu-Be source is a stainless steel cylinder 1.020 in. in diameter and 1.300 in. long containing an intimate mixture of 16 g of plutonium with 8–10 g of beryllium. Total neutron emission is 1.6×10^6 neutrons/sec.

The best moderators contain light atoms such as hydrogen or deuterium, to reduce rapidly the energy of the neutrons, and elements of low cross section, so that the neutrons will not be absorbed by the moderator before they can be useful. Graphite, heavy water (D_2O), ordinary H_2O and paraffin are used as moderators. The former two are preferred because they absorb a smaller fraction of the neutrons; however, the latter two are used for reasons of economy and ready availability.

The paraffin-moderated source was set up because it was realized that a number of institutions may not be able to purchase a subcritical reactor for such experiments. Also, it was expected that it would be possible to construct a suitable source assembly at low cost that would approach the same activity from irradiation of the same duration. The results indicate that this is possible and that this type of experiment could be performed in any school which had personnel licensed to handle the neutron source. The plutonium-beryllium source was loaned without cost to the University by the Atomic Energy Commission.

Preliminary Calculation Exercise

The neutron activation experiment was introduced during the lecture discussion of cross sections. The class was given a sample size (thickness and cross-sectional area), neutron flux and irradiation time. They were asked to find two isotopes that would give at least 100 disintegrations/min at the end of a 24-hr irradiation. This served the purpose of finding the common materials that would give a useful amount of activity, as well as providing an interesting problem to illustrate the use of these factors. To facilitate calculation and checking the results the following method of calculation in five steps was recommended:

I. Summary of initial data including all the above-mentioned items and the target material, density, formula weight, atoms per cubic centimeter, decay constant, partial and total cross sections, relative abundances of the various isotopes and half lives and type and energy of radiation. (This information can be found in the textbook.[1])

II. Neutron absorption was calculated using the simple relationship:

$$\text{neutrons absorbed} = At(I_0 - I) = AtI_0(1 - e^{-n\sigma_t x})$$

where A is the target cross-sectional area, I_0 is the incident neutron flux/cm², I is the transmitted flux, σ_t is the total cross section for the target material, and t is the time of irradiation.

III. Product isotopes produced:

$$At(I_0 - I)\frac{\sigma_p}{\sigma_t} \times \text{abundance} = \text{R}$$

where σ_p is the partial cross section for the production of the desired isotope, and R is the rate of production per total time t.

IV. Product isotope atoms present at the end of irradiation

$$N = \frac{R\,(1 - e^{-\lambda t})}{\lambda}$$

where N is the number of atoms present at the end of irradiation, t is the time of irradiation, λ is the decay constant and must be in the same units of time as used for R in R/λ and as used for t in $e^{-\lambda t}$.

V. Disintegrations/min

$$-\frac{dN}{dt} = \lambda N$$

where λ is the decay constant/min. This could be made the observed activity by introducing an appropriate detection coefficient C, then counts/min $= C\lambda N$.

A separate calculation was made for each product isotope on a form sheet provided.

For example we may make the calculations for the production of Cu^{64} in normal copper (II) oxide, CuO. The given conditions were:

Neutron flux: 10^5 n/cm^2-sec;
Irradiation time: 24.0 hr $= 8.64 \times 10^5$ sec
Target area $A = 1.00$ cm², target thickness $= 0.10$ cm
Detection coefficient $= 0.3000$

The appendix in the text[1] gives the following information.

$\sigma_{total} = 3.6$ barns $= 3.6 \times 10^{-24}$ cm²
σ_p for $Cu^{63} = 4.3 \times 10^{-24}$ cm²
Relative abundance of $Cu^{63} = 69.1\%$
Product half life ($t_{1/2}$) $= 12.8$ hr
Type and energies of radiation: β^- 0.571, β^+ 0.657 (note that both beta and gamma radiation will be observed since $\beta^+ +$ electron $\rightarrow 2\ \gamma$)

The handbook[2] values needed are:

Target (CuO) density: 6.40 (note that target material will not be packed in the holder this tightly, results will be high)
Target formula weight: 79.54

From this we can calculate the number of target atoms/cm³. The following relationship is used:

$$n = \frac{\text{density}}{\text{formula weight}} \times \text{Avogadro's number} \times \text{number of target atoms/molecule}$$

$$= \frac{6.40 \times 6.025 \times 10^{23} \times 1}{79.54} = 4.85 \times 10^{22} \text{ atoms cm}^{-3}$$

The decay constant λ may conveniently be used in days^{-1} for calculation of Cu^{64} atoms produced.

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{12.8\text{ hr}} = \frac{0.693 \times 24\text{ hr}}{12.8 \times 1\text{ day}} = 1.30\text{ day}^{-1}$$

For the disintegration rate λ is needed in units of min^{-1}

$$\lambda = \frac{0.693}{12.8\text{ hr}} \times \frac{1\text{ hr}}{60\text{ min}} = 9.02 \times 10^{-4}\text{ min}^{-1}$$

We next calculate the number of neutrons absorbed/unit time. Let the unit of time be the irradiation period, 24.0 hr.

$$\begin{aligned} At(I_0 - I) &= AtI_0(1 - e^{-n\sigma_t x}) \\ &= 1 \times 1 \times 24.0 \times 60 \times 60 \times 105(1 - e^{-4.35 \times 10^{22} \times 3.6 \times 10^{-24} \times 0.1}) \\ &= 8.64 \times 10^6(1 - e^{-0.0175}) \\ &= 8.64 \times 10^6(1.8 \times 10^{-2}) \\ &= 1.6 \times 10^7 \text{ neutrons absorbed/24.0 hr} \end{aligned}$$

Then we are ready for (III.), the product isotopes produced/unit time. To be consistent, let the unit time be the irradiation period.

[1] Friedlander, G. and Kennedy, J. W., "Nuclear and Radiochemistry," John Wiley & Sons, Inc., New York, 1955.

[2] Hodgman, C. D., "Handbook of Chemistry and Physics," 41st ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1959–60, p. 572.

$$R = At(I_0 - I)\frac{\sigma_{\text{partial}}}{\sigma_{\text{total}}} \times \text{abundance}$$
$$= 1.6 \times 10^7 \times \frac{3.6 \times 10^{-24}}{4.3 \times 10^{-24}} \times 0.691$$
$$= 9.3 \times 10^6 \text{ } Cu^{64} \text{ atoms produced in 24.0 hr}$$

Then (V.): Disintegrations/unit time at end of irradiation.

$$-(dN/dt) = \lambda N$$
$$= 9.02 \times 10^{-4} \times 5.20 \times 10^6$$
$$= 4690 \text{ disintegrations/min}$$

Assuming a detection coefficient of 0.3000

$-c(dN/dt) = c\lambda N$ = observed activity
= (0.3000) 4690
= 1407 counts/min observed from decay of Cu^{64} produced under these conditions.

Questions which arose from this problem gave an opportunity to discuss decay schemes (graphical representation of the types of decay, energies of radiation and properties of the different states) and isomerism (existence of an isotope in an excited state which decays by emitting a gamma ray to become less excited) as well as to ensure an understanding of the decay law, the concept of partial and total cross sections, rate of production of isotopes and the detection coefficient. The practical aspects of the problem were pointed out in the preparation of radioactive sources. The important factors in obtaining high activities after reasonable irradiation time were mentioned (large cross sections, large relative abundances and reasonably short half lives).

Typical discussion included: (1) an explanation of the identity of beta and gamma half lives in some cases and difference in others depending on the decay scheme; (2) explanation of isomerism and reason for observing two half lives from the decay of the product of irradiation of a single isotope (iridium served as a good example of this); (3) comment on the maximum amount of an isotope that could be obtained from a given set of conditions including geometry, neutron flux, and half life so that students could estimate the optimum irradiation time.

Table 1. Energy of Beta Emission from Neutron Irradiated Samples

Isotope	Literature value[a]	Energy (Mev), paraffin-moderated source	H_2O-moderated source
Br-80	1.99	1.85	1.841
Br-82	0.444	...	0.426
Dy-165	1.25	1.103	1.315
Mn-56	2.81	3.03	2.837
	0.65	0.679	...
I-128	1.13	1.214	0.98
	...	0.308	...
As-76	1.76	1.901	...
	0.36	0.421	...
	2.97	0.891	2.847
W-187	1.33	...	1.11
	0.63	...	0.51
Sb-122	1.40	...	1.28
Pr-142	2.17	2.044	2.146
	0.59	0.725	...
Cu-64	0.571	...	0.32
Y-90	2.26	...	2.463
Au-198	0.960	0.845	0.882
Na-24	1.39	...	1.22
La-140	1.67	1.598	1.580
	0.83	...	0.780

[a] *Rev. Modern Physics*, **30**, No. 2, Part II, 585–904 (April, 1958).

Experimental Procedure

After the calculations were completed approximately twenty suitable elements were listed which could be obtained in the stock room or adequate samples purchased for a reasonable price. Some of these could be handled easily and irradiated as the elements, while others were more readily available as compounds. Oxides, hydroxides, or oxyacids, and salts with other cations or anions of low cross section were used.

At first the samples were placed in glass vials with paraffin as a sealing material around the cork. This provided a liquid-tight container. However, in the process of neutron irradiation the glass became more active than the sample in a few cases. Therefore glass containers were not used and plastic vials made from polystyrene tubing were substituted quite satisfactorily. The sample holders were made by cutting pieces of $^5/_8$-in. o.d., $^1/_2$-in. i.d. polystyrene tubing in $2^1/_4$-in. lengths. Pieces of polystyrene $^1/_8$ in. long were cut from a rod $^1/_2$ in. in diameter and cemented in the bottom of the tube. A piece of $^1/_2$-in. polyethylene rod 1 in. long made a good stopper and was cemented in to make a liquid-tight container. The flat sample mounts were made by cutting $1^1/_8$-in. squares from $^1/_{16}$-in. thick Lucite sheets. One third of the squares had 1-in. diameter holes drilled in them. The drilled piece was centered on a plain square and cemented. In some cases these were used in a Nuclear Chicago model C110B automatic sample changer. The corners were cut to permit fitting in the sample holders. The sample material was placed in the depression in the plastic holder, then another plain square was placed on top and sealed with paraffin or thinned methyl methacrylate around the edges. This gave a three layer sandwich with the sample sealed in a circular central cavity 1 in. in diameter and $^1/_{16}$ in. deep. The cylindrical samples were placed inside a 1-in. o.d., $^3/_4$-in. i.d. polystyrene tube which had been sealed with a plug at the bottom. A lead weight was placed on top of the plug. A $^1/_2$-in. plastic rod was used as a spacer to center the samples vertically with the center of the Pu-Be sources. The plastic tube was placed inside one of the aluminum tubes normally used to hold uranium slugs. For the paraffin-moderated source the samples were placed in a similar but shorter plastic tube for irradiation. The flat samples for beta irradiation were sealed, wrapped with two rubber bands and placed in a polystyrene tube similar to that used to hold the cylindrical samples. Two slots were cut in the tube parallel to the axis so that the samples would be held in place facing the sources and centered on them. The sample holders were weighed before and after loading to obtain the weight of the irradiated sample.

After irradiation the samples were characterized by determining the type of radiation (alpha, beta or gamma), measuring the half life of the activity and also the energies of the radiations when possible. Alpha radiation (helium nuclei) has very short range and extremely thin window Geiger tubes or other devices (proportional counter, electroscope) must be used to detect this radiation. Thin aluminum absorbers placed between the sample and detector will absorb alpha particles. The scintillation detector with a sodium iodide crystal will detect only gamma radiation.

The Geiger tube is efficient for beta radiation but detects only about 1% of incident gamma radiation. A comparison of counting rates indicates the type of radiation.

Beta activity was measured using the flat samples with Geiger tubes of either 1.8-mg/cm² or 4.5-mg/cm² end window thickness. The samples were placed on shelves on a Lucite mount similar to that shown in the text,[1] p. 272, so that different geometries could be obtained, and so that Feather plot data could also be measured.

The samples for gamma measurement were used as they came out of the reactor. However, the samples for beta measurement had to be uncovered to reduce absorption due to the Lucite top. The rubber bands were removed, and a sharp spatula was used to break the paraffin or methacrylate seal and pry up the top of the sample holder.

For measuring gamma ray activity a well-type scintillation detector was used. Normal counting rates were measured with a Radiation Counter Laboratories model 11005 scintillation detector. Gamma ray spectra were obtained with a Baird Atomic spectrometer. Both of these used a sodium iodide, thallium activated crystal $1^3/_4$ in. in diameter and 2 in. high. The well size was $^5/_8$ in. in diameter by $1^1/_2$ in. deep.

The half life of the activity is determined by measuring the activity of a sample as a function of time. The relationship $A = A_0e^{-\lambda t}$ may be arranged to $\ln A/A_0 = -\lambda t$, where A is the activity at time t and A_0 is the activity at time t equals zero. From this it can be seen that a plot of the logarithm of the activity versus time should give a straight line. The time required for diminution of the activity by a factor of one half (half life) can be read directly from such a plot.

The Feather method for determining the maximum energy of a given beta radiation is described in many texts on radiochemistry. It involves the assumption that all beta ray spectra are similar in appearance (i.e., the percentages of beta particles having a given fraction of the maximum energy is constant from one type of beta emitter to another). Then some beta emitter whose maximum energy and range in aluminum absorbers is known is chosen as a standard (usually P^{32}). The logarithm of activity is plotted against the absorber thickness between the sample and Geiger tube. The thickness corresponding to the known maximum energy is used to obtain the maximum range. The range is usually divided into ten equal increments. The reduction in activity corresponding to 10%, 20%, etc., of the range in the absorber is read off from the plot. The per cent reduction in radioactivity corresponding to the 10%, 20%, etc., range is assumed constant for all beta emitters because of the assumed similarity in spectra. A similar plot of logarithm of activity of an unknown material versus the absorber thickness is made. The per cent reduction in activity obtained from the standard is used to find the thickness corresponding to 10%, 20%, etc., of the range. The apparent range is obtained by multiplying these thicknesses by the reciprocal of the range. For example, if 20% reduction corresponded to 50 mg/cm² of Al, the range would be $50 \times (100/20) = 250$ mg/cm² Al. The apparent range is plotted against the per cent of the range and extrapolated to 100% to obtain the maximum range. A range energy relationship such as

Table 2. Neutron Activation Samples Irradiated in Nuclear Chicago Model 9000 Subcritical Reactor

Target	Chemical form	Half life (lit.)	γ half life	β half life	Initial γ activity (counts/min)	Initial β activity (counts/min)	Irradiation time	
Nd	Nd_2O_3	2.0 h[a]	1.5 h	...	2,640	61	22 h 57 m	19 h 35 m
		15.0 m	...	15.4 m	...	...	...	...
Cu	Cu powder	12.8 h	12.8 h	11.7 h	31,000	350	22 h 57 m	22 h 45 m
La	La_2O_3	40.22 h	45.5 h	42.3 h	28,000	1,456	22 h 53 m	71 h 25 m
Sb	Sb_2O_5	2.80 d	2.83 d	2.65 d	12,500	630	22 h 53 m	27 h ...
I	KI	24.99 m	25.0 m	23.9 m	32,500	2,500	4 h ...	4 h 27 m
W	W metal	24.0 h	23.7 h	23.0 h	140,000	1,200	66 h 23 m	23 h ...
Ni	NiO	2.564 h	2.85 h	i.a.[b]	555	i.a.	23 h 15 m	22 h 45 m
Hg	Hg, HgO	24h, 65h	36.9 h	i.a.	1,400	i.a.	162 h 7 m	23 h ...
Au	$AuCl_3$, Au	2.647 d	2.9 d	2.44 d	2,400	2,780	162 h 7 m	43 h 40 m
Ce	CeO_2	8.7 h	10.3 h	i.a.	1,300	i.a.	22 h 53 m	47 h ...
Sm	Sm_2O_3	47.1 h	40.7 h	...	7,700	150	24 h 41 m	4 h 27 m
		23.5 m	...	22.4 m	...	...	...	...
Br	NH_4Br	17.6 m	2.6 h	21.1 m	33,300	3,900	24 h 9 m	71 h 25 m
		35.87 h	34.4 h	8 h	...	...	...	...
Zn	Zn dust	13.8 h	15.6 h	...	1,290	75	24 h 41 m	47 h ...
		57 m	...	1.67 h	...	...	...	...
V	V_2O_5	3.76 m	3.87 m	4.55 m	27,500	2,000	64 h 35 m	1 h 5 m
Ag	$AgNO_3$	2.3 m	1.85 m	2.0 m	13,600	1,100	19 h ...	1 h 30 m
		24.25 m	4.80 m	...	...	...	...	...
Co	Co_2O_3	10.47 m	72.3 m	i.a.	1,500	35	24 h 9 m	27 h ...
		5.24 y	...	...	...	...	...	...
Sn	Sn mesh	9.5 m	8.5 m	i.a.	1,140	i.a.	44 h 5 m	4 h 27 m
Na	Na_2CO_3	14.97 h	15.2 h	12.9 h	10,700	360	24 h 9 m	27 h ...
Mn	MnO_2	2.576 h	2.645 h	2.59 h	380,000	10,000	22 h 57 m	22 h 45 m
As	H_3AsO_4	26.4 h	26.2 h	25.7 h	52,000	6,500	7 d 2 m	44 h 35 m
Pr	Pr_6O_{11}	19.2 h	[c]	21 h	[c]	1,100	[c]	43 h ...
Y	Y_2O_3	64.2 h	[c]	65.5 h	[c]	460	[c]	91 h 55 m
Dy	Dy_2O_3	139.2 m	i.s.[d]	139 m	i.s.	3,300	i.s.	19 h 35 m
Cr	Cr_2O_3	3.52 m	[c]	i.a.	[c]	285	[c]	22 h 45 m

Mounting: Plastic. Location: About 0.5 in. of H_2O from source.
[a] h, hour; m, minute; d, day; y, year.
[b] i.a. = Insufficient activity.
[c] Sample not irradiated.
[d] i.s. = Insufficient sample.

Table 3. Neutron Activation Samples Irradiated in Paraffin-Moderated Source

Target	Chemical form	Half life (lit.)	γ half life	β half life	Initial γ activity (counts/min)	Initial β activity (counts/min)	Irradiation time	
Nd	Nd_2O_3	11.06 d	11.3 d	...	228	...	16 h 43 m	21 h 20 m
		2.0 h	...	i.a.[b]	195	i.a.	.. ..	.. ..
Cu	Cu powder	12.8 h	13.1 h	10.6 h	9,000	120	32 h ..	40 h 25 m
La	La_2O_3	40.22 h	43.5 h	41.5 h	25,200	310	119 h 41 m	48 h 49 m
Sb	Sb_2O_5	2.80 d	1.27 d	2.84 d	10,000	256	143 h 38 m	116 h 35 m
I	KI	24.99 m	26.2 m	21.7 m	6,100	200	4 h 32 m	3 h 49 m
W	W metal	24.0 h	23.9 h	24.4 h	30,000	130	72 h 12 m	46 h 53 m
Ni	NiO	2.56 h	i.a.	[c]	270	[c]	19 h 30 m	[c]
Hg	Hg, HgO	24h, 65h	?	[c]	500	[c]	144 h	[c]
Au	$AuCl_3$, Au	2.697 d	2.58 d	2.42 d	410	1050	143 h 54 m	131 h ..
Ce	CeO_2	8.7 h	9.75 h	[c]	1,200	[c]	96 h ..	[c]
Sm	Sm_2O_3	47.1 h	47.7 h	i.a.	2,900	i.a.	64 h 15 m	2 h 24 m
Br	NH_4Br	35.87 h	34.1 h	...	10,000	...	71 h 24 m	4 h 47 m
		17.6 m	...	14.7 m	...	165	.. ..	.. ..
Zn	Zn dust	13.8 h	13.7 h	[c]	610	[c]	120 h 17 m	[c]
V	V_2O_5	3.76 m	3.67 m	3.03 m	7,100	265	46 m	1 h 28 m
Ag	$AgNO_3$	24.2 s	18 s	32 s	10,200	410	48 m ..	1 h 56 m
		2.3 m	1.9 m	2.73 m	...	...	.. ..	.. ..
Na	Na_2CO_3	14.97 h	14.7 h	15.0 h	2,500	80	48 h 5 m	47 h 47 m
Mn	MnO_2	2.576 h	2.65 h	2.58 h	111,250	1850	16 h 5 m	18 h ..
As	H_3AsO_4	26.4 h	27.2 h	26.1 h	9,985	810	72 h 10 m	43 h 25 m
Pr	Pr_6O_{11}	19.2 h	[c]	18.5 h	[c]	570	[c]	48 h 23 m
Y	Y_2O_3	64.2 h	[c]	63.5 h	[c]	105	[c]	120 h ..
Dy	Dy_2O_3	139.2 m	[c]	140.6 m	[c]	9800	[c]	19 h ..

Mounting: Plastic. Location: About 1/2 in. from one-curie plutonium-beryllium source.
[a] h, hour; m, minute; d, day; y, year.
[b] i.a. = Insufficient activity.
[c] = Sample not irradiated.

$R = 542\ E - 133$, where R is the maximum range in mg/cm² of aluminum, and E is the maximum beta energy in million electron volts, is used to calculate the maximum beta energy.

Gamma ray energies were determined using a gamma ray spectrometer with a scintillation detector. The scintillation detector produces a flash of light from the interaction with a gamma ray. The light flash is detected by a photomultiplier tube which produces a small pulse. The pulse is amplified and sent to a scaler where it is recorded as a count. The gamma ray spectrometer analyzes pulses from the amplifier and essentially sorts them by means of electronic discriminators according to the energy of the gamma ray that produced the pulse. This spectrometer then indicates the amount of activity of different gamma ray energy that is emitted by a sample. Thus a maximum activity at a certain energy indicates that the isotope emits a gamma ray of that characteristic energy.

Another method for determination of gamma ray energy involves the determination of the gamma half-thickness. The interaction of gamma radiation with matter leads to a relationship of the type $\log A/A_0 = -\mu d$ where A_0 is the activity observed through an absorber of thickness d and absorption coefficient μ. The half-thickness is determined experimentally. Plots of half-thickness vs. energy of radiation for different absorbers are used to determine the energy from the half-thicknesses.

Results

Several means of identifying the products of irradiation were available and used. The properties that are frequently used are the half lives and energies of the radiations. The half lives were measured in the usual way and used as a preliminary identification.

Confirmation of the identification through measurement of the energies could be carried out in two ways. First, for the gamma active samples, an energy spectrum could be obtained on the spectrometer and compared with the decay scheme. This provided another good opportunity to examine and understand a decay scheme. In some cases individual peaks could be counted and their half lives determined where isomers or mixtures of isotopes were involved, for further identification. Secondly, range energy relationships could be used to determine the energies from ranges of beta emitters, and if cylindrical rather than well-type scintillation detectors were used, gamma energies would also have been measured this way.

The Feather method of comparing the activity vs. range plot of the unknown was used on the following samples: NH_4Br, Dy_2O_3, Mn, KI, H_3AsO_4, W, Sb_2O_5, Pr_6O_{11}, Cu, Y_2O_3, Au, Na_2CO_3, La_2O_5. These plots were compared with the data for phosphorus-32. Good agreement was obtained in most cases as seen in Table 1.

The relationship used to obtain the energies was range in Al (gm/cm²) = 0.542 max E (in Mev) − 0.133.

A summary of the data obtained from the samples used is given in Tables 2 and 3. It can be seen easily that there are a number of readily available materials that make reasonably active sources for student use.

Generally the agreement between the observed and expected half lives was very good. The student interest was good, and carried over into the classwork.

Acknowledgment

The author wishes to thank Herman Hein for carrying out much of the work reported here. This work was supported by the Atomic Energy Commission.

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Aspects of Advanced Training in Nuclear and Radiochemistry

In considering "advanced work" in connection with the place of nuclear and radiochemistry in a curriculum, the immediate question involves the practical training of non-professional technicians versus the training in techniques for a professional staff. Is it a function of a university to devote effort, time, money, and space for training technicians of the non-professional type in routine radiochemical operations for industrial and government agencies? Let us define next the probable types of clientele assigned to a university group for radiochemical training and/or education.

Also, under the category of "advanced work," serious thought should be given to the inclusion and extent of topics on radioactivity and radiochemistry in the traditional upper division courses such as physical, advanced analytical, and instrumentation courses.

These groups are: (*a*) advanced students in chemistry and physics, (*b*) advanced students from related fields such as soil science, engineering, horticulture, etc., (*c*) teachers attending teachers' institutes, (*d*) radiological monitoring workshop registrants, (*e*) technicians from service laboratories, (*f*) students from laboratories in foreign countries, etc.

From the concepts mentioned, it is obvious that "advanced radiochemical training" can be considered as (*a*) a training function for registrants needing only training in routine nuclear and radiochemical laboratory procedures, and (*b*) an advanced course for education in advanced chemistry. There is no argument that the latter is definitely a university educational responsibility. However, it could be debated whether or not a university has the function of training technicians in routine radiochemical procedures. For example, if a State Department of Education and the Civil Defense Agency plan a cooperative workshop on radiological monitoring to be given to high school science teachers, does the university proceed to give such a course? At Michigan State University such a workshop is given. It can be well argued that state-supported universities have certain responsibilities toward citizenship activity of this kind.

The responsibility of citizenship activity is a serious one which should not be dodged by scientists in the universities. After all, the layman and the lay scientist look and appeal to us for guidance in the treatment and handling of any dangerous material—it may be an explosive, a radiochemical, a toxic chemical, or a living organism. We *do* have a responsibility, but it must be viewed in a "level-headed" fashion. We must, on the one hand, emphasize and stress the dangers, the hazards of handling potentially dangerous materials (radiochemicals, poisons, explosives, etc.); and on the other hand, emphasize not going overboard on the opposite extreme of excess caution.

In changing our point of view, for the moment, to course content, we can state that the learning experience for technicians is basically a training function for which most of the time and the heavy emphasis is placed on laboratory techniques. For example, the type of radiochemical experience to be given teachers registered in the various teachers' institutes should be of the type which states what radioactivity and radiochemistry are, and should emphasize measuring techniques. By and large, this group of individuals is not prepared for the more rigorous type of radiochemistry training suitable for graduate students or others who will make regular use of the techniques of this field of chemistry as part of their everyday scientific work. The training for these teachers should be such that they in turn will have an adequate background to tell their pupils about the importance of radiochemistry and to answer many questions put to them by the layman.

However, the educational experience for advanced students involves not only considerable laboratory time but in addition, places emphasis on theoretical aspects and fundamental principles.

Under this heading of advanced students, it is also necessary to distinguish between the group of students in advanced courses, such as physical or analytical chemistry, who do not intend to pursue radiochemistry as an important activity and those students who will go into graduate study or to laboratories where radiochemistry plays an important role in the scientific programs.

For the advanced undergraduate we aim to give a description of the radioactive process, the radiations and their interactions with matter, and a brief survey of the more important applications of radiochemistry to chemical problems. In the laboratory, two to four experiments serve to illustrate detection and measurement of the radiations.

For the graduate student preparing himself to use radiochemical techniques and principles as an integral part of his daily job, the program should include a thorough and more rigorous discussion of radioactivity, production of isotopes, applications to chemical problems, and perhaps an introduction to some of the more relevant phases of nuclear physics and chemistry. For this group, the laboratory work after the first four or five experiments becomes less mechanical and more investigative in nature.

The courses in this last category given at Michigan State University are "Introduction to Radioactivity" in the Physics Department, "Radiochemistry" in the

Presented as part of the Symposium on The Place of Radioactivity and Nuclear Chemistry in the Curriculum, sponsored by the Division of Chemical Education, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

Chemistry Department, and "Radiobiology" in the Physiology and Pharmacology Department. The first of these three courses stresses elementary nuclear properties and processes and emphasizes the nature of radioactivity and its measurement at the advanced undergraduate level. Special attention through experiments with radioisotopes and their associated radiations provides the physical background for biological and industrial applications. The graduate level radiochemistry course considers the principles of radioactivity, the chemistry of production, isolation, and identification of radionuclides and their uses in chemical research. In the third course, radioactive tracer techniques are applied to the study of biological functions and to the control of radiation hazards.

These three courses are designed to meet the needs of advanced students in chemistry, physics, engineering, and the biological and agricultural sciences. The chemistry and physics courses are taken by high school and junior college teachers who have adequate backgrounds.

However, a new course is contemplated and needed for those teachers and others whose previous educational experience would not qualify them for the existing courses. This new type of course should emphasize the "what" of radiochemistry rather than the "why." It should answer the "what" of the radioactive process and measurements and should describe the practical application of radiochemistry to industrial, physical, and biological sciences. A laboratory program should be included to illustrate common measuring techniques and some simpler applications of radioactivity. This group would be competent to make simple demonstrations to students and to do Civil Defense monitoring. For a group of this sort, the mathematics requirement should not be so stringent as to eliminate the average high school science teacher. It is not implied, however, that experiments for this group are not to be quantitative.

Teaching Students to Use Radiochemistry

The radiochemistry course at Michigan State University is taken by advanced students preparing to use radiochemistry in their research programs and later scientific endeavors.

In the discussion portion of this course, a rigorous approach but one which does not presuppose a study of nuclear physics is taken. Major topics are the nature of radioactivity, the interaction of radiations with matter, the statistics of the radioactive process, the physical chemistry of tracer concentrations, the non-trivial applications of radioactivity to chemical problems, nuclear reactions and isotope production, and an introduction to the problem of nuclear stability.

In the parallel laboratory program, it is presupposed that the student has not only a knowledge of but also considerable competence in chemical operations and manipulations. For example in the ten-week program at M.S.U., four experiments are devoted to measurement procedures including statistical aspects. These experiments also serve to introduce the student to separations at the tracer level. Two experiments expand the experience in tracer chemistry including the physical chemistry at low concentrations. The remaining four experiments deal with specific applications such as isotopic exchange reactions, solvent extraction, solubility determinations, etc. These latter experiments are modified to meet the needs of the groups of students involved and the availability of isotopes at the moment. In these latter experiments, particular emphasis is placed on demonstrating to the student that great care is necessary in handling radiochemicals, that quick and accurate work is necessary, that there are hazards, that it is possible to work with minute quantities, and that the radioactive process is a valuable scientific tool.

It must be considered, for experiments in this category, where and how radioisotopes can be obtained. For example, if means of producing appropriate radioisotopes such as a cyclotron or reactor are not available, recourse to other sources is necessary. Isotopes can be secured from Oak Ridge and other groups. For the work at Michigan State University, where a source of irradiation is not available, we use natural uranyl nitrate as a source of Th^{234} (25d) and Pa^{234} (68s). The shortest half-life material which we commonly purchase is I^{131}(8d). Other tracers purchased range in half life from several weeks to twenty years.

We have hinted that there are many facets to the problem of teaching radiochemistry. Is it necessary that every undergraduate working for a baccalaureate degree be indoctrinated in the concepts of radiochemistry through the media of experiments and lectures injected into their programs? If radiochemistry is included, is it to be a separate or integral part of physical, analytical, or some other area? Or should there be a separate course to teach the simplest theory and experimentation of radiochemistry? Should this course serve the student preparing for a professional career in chemistry as well as for the persons planning on technical sales, scientific literature, etc., as future activities?

It is our feeling that a special course in radiochemistry should be restricted to the graduate level and gauged for the individual primarily planning to use radiochemistry as a strong tool in his professional field. We feel also that for the student planning on chemistry as a background for a semiprofessional scientific job, e.g., technical sales, radiochemistry should be taught in some of the undergraduate courses. Arguments can be advanced for including the information on this area in either undergraduate physical or analytical chemistry. It seems logical since radiochemistry in these programs will deal primarily with the techniques and the analytical applications, that the material most properly belongs in one of the analytical courses, preferably in the course in instrumentation. Any such training, of course, seems scarcely suitable for a sophomore analytical course. Since radiochemistry represents a branch of analytical chemistry on a par with polarography, spectroscopy, etc., it is desirable to make room in the program for it. The inclusion of radiochemistry necessarily reduces the time available for those topics now considered essential in the analytical course. This, in turn, raises the question whether or not the basic analytical sequences should be drastically overhauled with the idea of teaching the important principles with newer techniques since so many new methods of analyses utilizing newer electronic equipment, etc., are becoming available.

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Solubility of Neodymium Oxalate by Coprecipitation with Pm-147

Radioactive tracers are becoming increasingly useful in the determination of the solubility of various substances. For the determination of the solubility of very sparingly soluble compounds, the radioactive tracer technique often represents the only practical method. Unfortunately it is not always possible to obtain readily a radioisotope with a convenient half life. If, however, a radioisotope of another element of closely related chemical properties can be substituted, coprecipitation may tend to distribute the tracer element between the solution and solid phases in the same proportion as the carrier. In such a favorable case, only the residual radioactivity of the solution due to the tracer need be measured to give information on the solubility of the carrier.

The relationship may be expressed as follows:

Let
S = solubility of carrier salt, mg/ml
T = initial tracer added, dpm/ml
x = initial carrier concentration, mg/ml
y = tracer left in filtrate, dpm/ml

If the coprecipitation distribution factor = 1, then

$$\frac{\text{carrier (soln.)}}{\text{carrier (ppt.)}} = \frac{\text{tracer (soln.)}}{\text{tracer (ppt.)}}$$

$$\frac{S}{x - S} = \frac{y}{T - y}$$

Since S and y are small compared to x and T, respectively,

$$xy = ST \qquad (1)$$

In the ideal system, therefore, a summation of x, y points at a fixed T would constitute a rectangular hyperbola on linear coordinate paper or a straight line of unit slope on a log log plot. If the experimental results are found to take this form it would indicate that the tracer does coprecipitate with the carrier with a distribution coefficient of 1. Moreover, the carrier solubility (S) could then be determined from the xy product, according to equation (1).

This paper describes a measurement of the solubility of neodymium oxalate by coprecipitation with promethium-147. This experiment illustrates the method suggested above, and by comparison with the known value, permits an evaluation of Pm-147 as a general tracer for neodymium and possibly other rare earths.

Neodymium oxalate (2–100 mg) was precipitated from an excess of aqueous oxalic acid containing Pm-147 by adding neodymium chloride in solution, the total volume being 25 ml. The reaction mixture was warmed to 80° for an hour and allowed to stand at room temperature overnight. The precipitate was then separated by filtration and aliquots of the filtrate were evaporated on planchets for counting. Because of the very slight solubility of the oxalate, it was necessary to use a relatively high concentration of the Pm-147 tracer: usually one-half millicurie per determination, or 5×10^7 dpm/ml before precipitation. This resulted in 10^4 to 2×10^5 dpm/ml in the filtrate, depending on the initial amount of neodymium added.

The oxalic acid concentration was high enough ($0.1M$) to insure a fairly constant excess at all neodymium levels. This was necessary so that each filtrate aliquot would have about the same self-absorption counting correction. Under the conditions employed, the thin (1 mg/cm²) layer of oxalic acid on each planchet reduced the apparent counting efficiency to about one-fourth of that of a weightless sample. Blank determinations to establish the counting correction were an essential part of the experimental program.

Table I. Results of Solubility Determinations

Pm-147 tracer, Dpm/ml × 10^{-7} (T)	Nd^{+3} Carrier, mg/ml (x)	Net activity in filtrate (1 ml) Cpm × 10^{-3}[a]	Net activity in filtrate (1 ml) Dpm × 10^{-3} (y)[b]
5.0	0.40	1.35	54
5.0	0.40	1.37	55
5.0	0.20	4.13	165
5.0	0.80	1.92	(Omitted)
2.5	0.12	2.17	87
2.5	0.40	0.60	24
2.5	1.60	0.20	8.0
5.0	0.20	4.80	(Omitted)
5.0	0.40	1.12	45
5.0	0.80	0.56	22
5.0	1.60	0.41	16.4
5.0	0.008	5.35	214
5.0	2.00	0.39	15.6
5.0	4.00	0.28	11.2

[a] Average of three or four planchets, corrected for background.
[b] Counting efficiency = 0.025 for planchets containing about 8 mg of oxalic acid.

The result of a series of precipitations carried out starting with 0.56 mc of Pm-147 each are given in Table 1 and plotted with log log coordinates in Figure 1. The best straight line fitting the experimental x, y points (x = mg/ml of neodymium before precipitation, y = dpm/ml of Pm-147 in filtrate) had a slope of 1.15 in fair agreement with the value of 1.0 implied by equation (1). The xy product common to all points on the best unit slope (dashed line) was 2.5×10^4 mg-dpm/ml². The solubility (S) was derived from equation (1).

$$xy = ST = 2.5 \times 10^4$$

Since $T = 5.0 \times 10^7$ dpm/ml,

$S = 5.0 \times 10^{-4}$ mg/ml $= 3.5 \times 10^{-6}$ mole/liter of Nd^{+3}

[1] Present address: Frick Chemical Laboratories, Princeton University, Princeton, N. J.

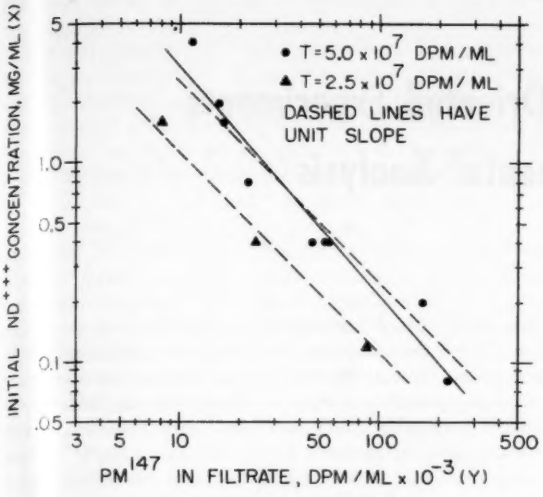

Figure 1. Log log plot of solubility data.

Some additional points were obtained with half the initial Pm-147 content, or 0.23 mc/25 ml. The xy product common to all points on the best unit slope was 1.1×10^{-4}, leading to a value of 3.1×10^{-6} mole/liter for S. These results are good approximations of the solubility of Nd^{+3} in unbuffered 0.1M oxalic acid solutions.

Using Nd-147 as the tracer, Crouthamel and Martin[2] found a minimum solubility of 1.5×10^{-6} mole/liter at an oxalate activity of 10^{-4}. Under the conditions reported here the oxalate ion activity would be approximately 10^{-5}, which corresponds to a Nd^{+3} solubility of 3×10^{-6} mole/liter.[3]

Apparently the coprecipitation of promethium and neodymium oxalates was very nearly ideal (i.e., the distribution coefficient between the solid and solution phases equals 1.0). This is not surprising considering that the two salts must have very similar crystal structures and solubilities. It would certainly be of interest to measure the solubilities of some other rare earth compounds using this tracer. Where great accuracy is not required, it may often be convenient to employ Pm-147 instead of a tracer radioisotope of the same element for the preliminary study of a new compound in the lanthanide series.

Due to the weak (0.22 Mev) beta emission, there is essentially no external radiation from glass vessels containing millicurie amounts of Pm-147, yet a G-M counter detects millimicrocurie amounts on a planchet with ease. Stock solutions need rarely be assayed, due to the chemical stability in weak acid and the long half life (2.6 years). This isotope is attractive from a safety standpoint, and very liberal tolerances have been established for ingestion.[4] The metabolism of rare earths is such that an accidental ingestion of as much as 10 mc of Pm-147 would scarcely lead to the permissible body burden being exceeded.

[2] Crouthamel, C. E., and Martin, D. S., *J. Am. Chem. Soc.*, 73, 569 (1951).
[3] *Ibid.*, p. 572, Figure 2.
[4] U. S. National Bureau of Standards Handbook 69, p. 61.
[5] Feibush, A. M., Rowley, K., and Gordon, L., *Anal. Chem.*, 30, 1605 (1958).

Assays

The aluminum planchets had a circular depression 1.25 in. in diameter and 0.1 in. deep. They were counted in close proximity to an Anton 210T G-M tube, on the top shelf in a lead-shielded sample chamber, with about 0.1 in. clearance from the end-window. Five-minute counts were recorded on an Atomics 1040A scalar for all planchets. The background, usually 25–30 cpm, was subtracted. Table 1 gives the net counts and corresponding assays for fourteen determinations.

The stock Pm-147 solution was assayed by comparison with a known standard, and found to have 28 ± 2 microcuries/ml. When an appropriate dilution was counted under the same conditions used for the filtrate aliquots in the solubility determinations, it gave 10% of the calculated decomposition rate, or a counting efficiency for a weightless sample of 0.10. A number of additional planchets were prepared with this same dilution plus 8 mg of oxalic acid (equivalent to 1.0 ml of the 0.1 M filtrate). The average count rate then observed was reduced by a factor of four to the equivalent of 2.5% of the theoretical, with a precision of 0.5%. Assays of filtrate aliquots were therefore made by dividing the measured cpm by a counting efficiency correction factor of 0.025, and the reported dpm values may be considered precise to ±20%, a source of error due primarily to the variations in self-absorption of the oxalic acid residue in the planchets.

Referring to Figure 1, the filtrate activity point at 4 mg/ml of Nd^{+3} lies above the best slope fitting the remaining points. At this concentration level about half of the oxalic acid was carried out with the precipitate, and the remainder on the planchet was therefore only about 4 mg. The counting efficiency for such a case was not measured, but it would undoubtedly be higher than 0.025. It is evident that a more accurate assay correction factor would tend to make this experimental point a better fit to the theoretical unit slope.

Coprecipitation Theory

Recent work in the field of coprecipitation of rare earth oxalates has been summarized by Feibush, Rowley, and Gordon.[5] These authors discussed the experimental results in terms of a model in which the solution was in equilibrium with the surface of the growing crystal, not the entire solid phase. The corresponding distribution coefficients were constant over a wide range of tracer/carrier ratios at low concentrations. However, these coefficients were not in agreement with the calculated values derived from the known solubility products, nor were they always mutually consistent. Thus, the product of the Nd/Yt and Yt/Ce factors should have equalled that of Nd/Ce, which was not observed. In addition, the distribution coefficients were significantly affected by the rate of the reaction, and most of the data were gathered at concentration levels where the precipitation was incomplete even after several days. The present investigation indicates that in the limiting case of immediate and essentially quantitative precipitation, the Pm/Nd distribution factor is a constant approaching 1.0.

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Research-Oriented Experiments in Instrumental Analysis

The primary function of a course in instrumental analysis should be to introduce the student to the important instrumental methods and their particular advantages for research as well as analysis. Modern chemists more and more need a fundamental appreciation for the powerful tools which are available for their research. The student should acquire an understanding of these methods and their limitations from a well-designed laboratory course in instrumental analysis, rather than get a superficial knowledge of an instrumental technique at the time he finds it essential to his research. The latter approach is all too common today and causes a wasteful and inefficient utilization of modern chemical instrumentation. Such haphazard use of instruments leads either to an over-reliance on the data obtained or a misapplication of the instrumental method which gives useless, or at best confusing data. The chemist with a more basic appreciation for the particular advantages as well as limitations of an instrumental method and the chemistry related thereto can efficiently and more properly apply it to the solution of his problem.

Scope of Experiments

Although numerous texts have appeared in the last decade which discuss instrumental methods, the general absence of a challenging, reliable, and really instructive group of experiments in this field has caused many instructors concern. This serious deficiency has led to the development of a group of laboratory experiments which are designed to give a basic understanding of the theory as well as to demonstrate the importance of instrumental methods to the modern chemist. The experiments are planned not only to illustrate analytical applications for instruments but also, whenever possible, to apply instrumental methods to the evaluation of physical chemical data. This latter feature helps to insure that the student acquires a knowledge of the chemical principles involved in the measurement and, in many cases, aids him in selecting the most appropriate conditions for an analysis. A prime requirement for each experiment has been that it be well tested and workable. Laboratory procedures for many of the experiments have been written in a manner which forces the student to think about the basic principles of the method, rather than just "cookbooking" the experiment.

The group of some 40 experiments is divided into five sections; *Electrometric Methods* covers potentiometric, conductometric, voltammetric, and electrolytic methods; *Optical Methods* covers absorption and emission spectrometric methods; *Separation Methods* covers chromatographic and ion exchange methods (with chelometric titrations as a finish); *Radiochemical Methods* covers instrumental methods based on nuclear radiation; and *Instrumentation* contains experiments which demonstrate the characteristics and properties of electronic components and the general principles of instrument design. For each experiment the basic instrumental theory and chemical principles upon which it is based have been outlined; hence laboratory experiments may be assigned for periods prior to lectures on that subject. A preliminary report to be submitted before performing the experiment is suggested to insure that the student gains sufficient basic knowledge to undertake the experiment with profit. At the end of each experiment a set of more detailed questions is given which test the student's understanding and appreciation for the specific instrumental techniques. Additional experiments are also suggested with references for the use of superior students; it is required that they work out the details for themselves, i.e., as a minor research project. However, for the majority of students it is essential that they first gain familiarity and understanding of an instrumental technique by doing a well-tested experiment with detailed instructions. The authors assign a few periods near the end of the course during which the student carries out a minor research-type problem applying his knowledge of instrumental methods to a project in which he is interested.

Because there is only a limited amount of laboratory time available in any course, efficient use of it is imperative. To provide a maximum amount of time for actual use of an instrument, sample preparation has been minimized as far as possible.

Although ion exchange, chelometric, chromatographic, and non-aqueous methods are often not classified as strictly instrumental techniques, these methods are of extreme importance to the modern chemist. Most undergraduate programs do not introduce the student to these techniques, or if they do, it is a superficial, non-laboratory presentation. These methods can quite logically be made a part of a course in instrumental analysis. Again we feel that a student can only appreciate the importance and usefulness of such methods by actual laboratory experience.

Typical Experiments

Space does not permit a detailed discussion of the group of experiments. However, the philosophy be-

Presented as part of the Symposium on Educational Trends in Analytical Chemistry, sponsored jointly by the Divisions of Chemical Education and Analytical Chemistry, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

hind the entire group can be demonstrated by a few representative examples.

The *p*H titration of mixed phosphates is a common laboratory experiment in quantitative or instrumental analysis courses. Generally, this experiment is used to demonstrate only the simultaneous determination of a mixture of acids; however, sufficient data are taken in recording the titration curve to permit evaluation of the three ionization constants for phosphoric acid. Although the technique of analyzing multicomponent mixtures is important to the research chemist, of even greater importance is an understanding of the methods for evaluating the dissociation constants of acids and bases. Furthermore, a fuller understanding of solution equilibria is required of the student to carry out such an evaluation. Thus, for the same amount of time in the laboratory, the student may be introduced to two useful concepts for research, analysis of multicomponent mixtures and evaluation of dissociation constants.

An experiment in polarographic analysis is a standard part of most instrumental analysis courses. However, in the majority of cases the sole purpose of such an experiment is to demonstrate that certain metal ions under particularly idealized conditions can be identified and quantitatively analyzed at millimolar concentration levels. The student is usually impressed with the sensitivity and convenience of the method for such analyses, but he rarely gains any appreciation of the usefulness of polarography in chemical research. Frequently the student performs the experiment with "blind faith," not really understanding the basic principles of the method, and concludes at the end of the experiment that if he ever goes to work in a control laboratory it might be useful to look into the method again. We believe that experiments in polarography and related methods are important, that they can demonstrate many electrochemical principles, and that they warrant sufficient laboratory time for the student to gain a basic understanding of the methods and their applications. Table 1 lists several experiments which have been developed in an effort to accomplish these goals. These experiments demonstrate the basic principles of polarography and introduce the student to the common methods of polarographic analysis, both organic and inorganic. An additional experiment introduces the use of polarography for the determination of the formulas and stability constants of complexed metal ions. The latter experiment is much more closely related to an actual research application of the method than is some routine analysis of a metal ion. Furthermore, an experiment on complex ions serves to show how supporting electrolytes (complexing agents) can be employed to shift half-wave potentials in order to eliminate otherwise overlapping polarograms.

Table 1. Experiments for Polarography and Related Methods

Polarography: effect of oxygen; maxima; verification of the Ilkovic equation; verification of the potential-current equation; methods of quantitative polarographic analysis.
Polarography of organic compounds; nitrobenzene; effect of *p*H.
Determination of the formulas and stability constants for complexed metal ions; lead oxalate.
Amperometric titrations at the dropping mercury electrode; selection of potential.
Amperometric titrations at the rotating platinum electrode; relation between amperometric and potentiometric titrations at a polarized electrode.
Dual polarized electrodes for end-point detection; at constant current; at constant potential; reversible and irreversible electrode systems.

Several experiments involving amperometric methods are also listed in Table 1. The general aspects of polarized electrode systems are illustrated as well as conventional amperometric titrations.

Colorimetric and spectrophotometric experiments are also commonly a part of an instrumental analysis course. These experiments range from the determination of manganese in steel with a Duboscq colorimeter to the simultaneous determination of several components in a mixture using a recording spectrophotometer. Regardless of the particular experiment the main, and usually the sole, emphasis has been directed toward quantitative analysis as the ultimate end. Although spectrophotometric (and colorimetric) methods are extremely useful for analysis, this is only one of several important uses to which a future research chemist should be exposed.

Quantitative spectrophotometric analysis may on occasion be of interest to the organic chemist, but by far his greatest use of spectrophotometric methods in research is as an aid to structure elucidation. The inorganic chemist likewise will frequently use spectrophotometric methods in his research, but primarily as a means of determining formulas and evaluating stability constants. For many chemists a spectrophotometer is most useful as a means of following the kinetics of a reaction.

If it is agreed that quantitative analysis is only one of numerous important research applications of spectrophotometric methods, then it follows that these other applications should be made a part of the instrumental analysis course. The diverse applications of spectrophotometric methods give support to the conclusion that the major responsibility of a course in instrumental analysis should be to give the student an appreciation of the principles of the method as well as its limitations. Thus, an experiment which demonstrates the function of the various components of a spectrophotometer and how these may be adjusted to provide better data is far more useful than, say, the analysis of an unknown steel colorimetrically.

Many instructors will agree that more instructive experiments in spectrophotometric methods are desirable, but will also contend that the cost of expensive spectrophotometers prevents the implementation of such experiments. Certainly precision research spectrophotometers are too costly to be used on a large scale in an instrumental analysis course. However, the fundamentals and applications of spectrophotometry can quite adequately be demonstrated using the relatively inexpensive Bausch and Lomb Spectronic 20 Colorimeter. This instrument is actually a simple spectrophotometer which uses a grating as a dispersing agent. Its very simplicity makes it ideal for an instrumental analysis course and enables the student to understand the optical system easily and relate this to the basic principles of a spectrophotometer. Table 2 lists a group of experiments which have been developed to illustrate the basic principles of spectrophotometry and many of its applications in research. Interestingly, all of the experiments listed in Table 2 can be done

using a Spectronic 20 and, in fact, have been written for this instrument.

Table 2. Spectrophotometry Experiments using a Spectronic 20

Spectronic 20 colorimeter; theory, operation, and response; visible spectrum; absorption spectrum.
Beer's law; experimental verification; study of chromium (III).
Simultaneous analysis of a two-component mixture; cobalt (II) and chromium (III).
Desirable and undesirable colorimetric properties; iron (III) thiocyanate system; iron (II) orthophenanthroline system.
Precision colorimetry; high absorbancy method.
Photometric end-point detection; titration of a calcium-copper mixture with EDTA.
Determination of the pK_a of an indicator; Bromphenol blue.
Tristimulus colorimetry.

Additional experiments which illustrate the characteristics and use of infrared and ultraviolet spectrophotometers are desirable and have been developed for these instruments. The infrared experiment emphasizes structure elucidation and the qualitative identification of organic compounds. Various sample techniques are also illustrated. The experiments for ultraviolet spectrophotometry demonstrate its use for the analysis of multicomponent organic mixtures, and also for the determination of the formula and stability constants of complexed metal ions.

The experiments in the last section of the group are concerned with instrumentation. The many complex research instruments which are now in common use serve as a reminder that some appreciation of electronic components and circuits is desirable for chemistry students. We are not suggesting that the modern chemist should design and build his own instruments (although many do), but only that he should have some appreciation for what constitutes good instrument design. Experiments have been developed which demonstrate the characteristics and applications of various electronic components and circuits. Operational studies are made of several vacuum tubes as well as other components; in addition, simple measuring devices are assembled and tested using these components. Such experiments help destroy the fear and lack of confidence which many students have towards electronics.

The above examples should illustrate the general philosophy which has guided the development of the entire group of experiments. This philosophy has been that the experiments in an instrumental analysis course should provide the student with an appreciation of instrumental methods and their usefulness, as well as limitations, in chemical research. We believe that experiments of this type will bring about greater support and interest on the part of the students and, as is often equally important, that of the entire chemistry staff.

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A Useful Glass-blowing Lathe for Small Equipment

One of the principle difficulties in attaching a glass joint or tube to a spherical glass surface, particularly when an accurate common axis with an existing aperture is required, is the precise alignment of the new aperture with the existing one. This problem is solved in the professional glass-blowing shop by the use of a glass-blowing lathe, a machine item which is not ordinarily available in the laboratory to the practicing chemist who has an immediate, small glass-blowing job with such requirements.

In connection with meeting the latter need, we have found that the now commonly employed vacuum rotary evaporator (e.g., Rinco, Model 1007; Labline, No. 5100) serves as a useful and satisfactory small glass-blowing lathe. This piece of equipment, provided with a metal standard taper joint which rotates at about 75 rpm, has an outlet arm (i.e., the vacuum take-off) which is perfectly suited for the attachment of a rubber tube suitable for blowing an attached piece of rotating glassware. The use of a rotary evaporator in this capacity with a hand-torch or stationary glass-blowing burner readily insures the location of a proper sized hole accurately aligned with the existing standard taper neck in a flask or other piece of apparatus which is being modified. The use of carbon shapers with such a simplified glass-blowing lathe permits the construction of completely symmetrical in-line holes of any desired reasonable size, as well as the very simple alignment of tubes or joints attached to such holes.

The fact that a rotary evaporator may be mounted on a ringstand with its axis of rotation immediately adjustable from a horizontal to vertical position gives this piece of equipment a working versatility not shared by larger, commercial glass lathes. The accompanying photograph illustrates the use of a Rinco rotary evaporator as a small glass-blowing lathe in the horizontal position.

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Illinois Institute of Technology
Chicago 16

Solvents of High Proton Availability

My primary interest is kinetics, and some twenty-five years ago I attempted some kinetic studies in nonaqueous solvents with relatively little success; the difficulty was that we knew very little about the species present even in such common solvents as sulfuric acid. This led to some equilibrium studies in the solvent anhydrous hydrofluoric acid. Like water and sulfuric acid this solvent has a hydrogen-bonded structure and has a high dielectric constant ($\epsilon = 84$ at 0°C). Both H_2SO_4 and HF differ from water in that the proton availability is higher and in addition to protonating many oxygen and nitrogen compounds they protonate some aromatic compounds to an appreciable extent (*1*). Sulfuric acid has the disadvantages that some organic compounds are sulfonated in it, and that its self-dissociation is too high to permit use of conductance measurements to determine equilibrium constants (*2*).

In highly acidic solvents even the strong acids of aqueous systems become weak acids, the weaker acids become nonelectrolytes, and weak acids act as bases (proton acceptors).

Hydrofluoric Acid

Let us consider the HF system. In analogous fashion to water, one molecule of HF acts as an acid (proton donor) and loses a proton to another HF molecule acting as a base (proton acceptor) and

$$HF + HF \rightleftarrows H_2F^+ \text{ and } F^- \qquad (1)$$

Thus we have a new acid, a proton solvated with HF, and a base F^- which is also solvated with HF to form HF_2^- and higher solvates such as $H_2F_3^-$, $H_3F_4^-$ ... $H_{n-1}F_n^-$. Anhydrous hydrofluoric acid is a highly associated liquid, and both the cation and anion will be solvated. Equation (1) is a simplified statement of the process called "autoprotolysis." If we now introduce a fluoride acceptor, which we call a co-acid, such as BF_3, SbF_5, BiF_5, NbF_5, TaF_5, or TiF_4, reaction (2) takes place, e.g.,

$$F^- + BF_3 \rightleftarrows BF_4^- \qquad (2)$$

and the concentration of the solvated proton and acidity are increased (*3*, *4*, *5*). All of the above fluorides are covalent compounds. The ionic fluorides such as NaF would act as bases and decrease the acidity (*6*), as fluoride ion is the analogue of hydroxyl ion in aqueous systems.

If a methyl-substituted benzene is introduced into anhydrous hydrofluoric acid, the aromatic compound exhibits basic properties in accordance with the reaction

$$Ar + HF \rightleftarrows ArH^+ + F^- \qquad (3)$$

That the methylbenzenes are bases has been shown by the conductance method, the equilibrium constant for reaction (3) increasing from less than 10^{-8} for benzene to 10^{-2} for hexamethylbenzene. Addition of co-acids such as BF_3 and NbF_5 will displace reaction (3) to the right, increasing the concentration of ArH^+ just as the concentration of H_2F^+ is increased by equation (2). The species ArH^+ is regarded as the precursor in the isomerization or disproportionation reactions which take place when the methyl-substituted benzenes are dissolved in anhydrous hydrofluoric acid, and since the addition of co-acids (BF_3 etc.) increases the concentration of ArH^+ and the rates of these reactions (*7*), they are called co-catalysts. There should be a correlation between the equilibrium constants of reaction (2) and the velocity constants for isomerization.

Sulfuric Acid

Similar considerations should hold for the high-dielectric-constant solvent, 100% sulfuric acid, but the kinetics are complicated by sulfonation. Here we can write

$$\begin{array}{l} H_2SO_4 + H_2SO_4 \rightleftarrows H^+ \cdot H_2SO_4 + HSO_4^- \\ \qquad\qquad\qquad\qquad\qquad\qquad + \\ \qquad\qquad\qquad\qquad\qquad\qquad SO_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad \Downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad HS_2O_7^- \\ \qquad\qquad\qquad\qquad\qquad\qquad + \\ \qquad\qquad\qquad\qquad\qquad\qquad SO_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad \Downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad HS_3O_{10}^- \end{array} \qquad (4)$$

with SO_3 as the bisulfate-ion acceptor. That the addition of SO_3 actually increases the acidity is shown in Figure 1. (The acidity function H_0 will be discussed later.)

We are beginning just now to have sufficient knowledge of the species present in vitriol and oleum from the Raman spectra measurements of Young and his coworkers (*8*), and sufficient knowledge of the activity coefficients from the work of Giauque and co-workers (*9*), and of Gluekauf and Kitt (*10*), together with data from Deno and Taft (*11*), Wyatt (*12*), and others. Young and Walrafen (*13*) report the species HSO_4^-, H_2SO_4, $H_3SO_5^+$ for vitriol and $H_2S_2O_7$, $HS_2O_7^-$ and SO_3 for oleum and $SO_4^=$ for solutions below 12 *M* H_2SO_4. In addition there must be present the water-solvated proton usually written as H_3O^+, although there are probably three additional water molecules associated with the proton; and the sulfuric-acid-solvated

Based on a paper presented as part of the Symposium on Nonaqueous Solutions before the Division of Inorganic Chemistry, at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

proton $H^+ \cdot H_2SO_4$ and possibly the SO_3-solvated proton HSO_3^+. We regard the species $H_3SO_5^+$ as a proton solvated by both water and sulfuric acid molecules. Young and Walrafen did not find the species $HS_3O_{10}^-$

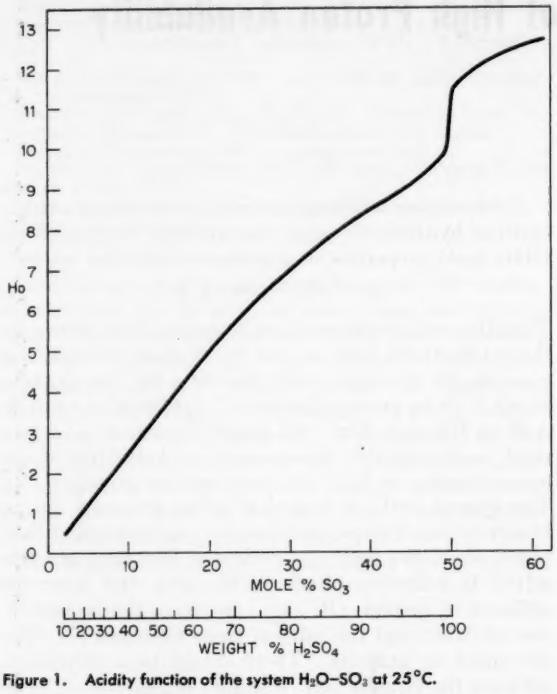
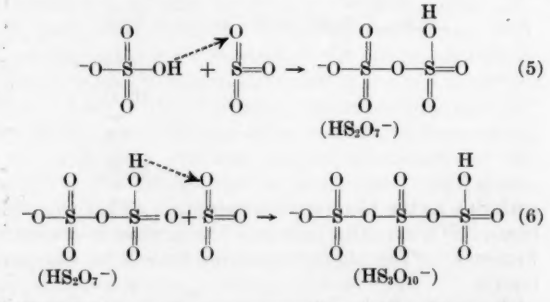


Figure 1. Acidity function of the system H_2O–SO_3 at 25°C.

which would result from the addition of a second molecule of SO_3 but under certain experimental conditions this reaction must occur for it is known that oleum polymerizes to a liquid and at least one asbestos-like solid product. These could result from a continuation of reaction (4) the final product being



(5)

(6)

$H(SO_3)_nSO_4^-$ or the corresponding acid. It is of interest that sulfur trioxide vapor does not polymerize and that samples of the dry liquid are stable over long periods of time when kept above the freezing point of the sample. Once frozen the sample rapidly polymerizes and heating to higher temperatures under pressure is required to reconvert the asbestos-like solid to the liquid polymer. The asbestos-like solid polymer probably has a cross-linked structure. The importance of liquid sulfur trioxide as an industrial sulfonating agent has led to many patents on inhibitors of polymerization (*14*). One commercial product called Sulfan B contains B_2O_3 as an inhibitor. Gillespie (*15*) has reported an acid $H[B(HSO_4)_4]$ formed when B_2O_3 is dissolved in oleum. Since Young and Walrafen (*13*) prepared their oleum solutions from Sulfan B the samples contained a small amount of the B acid and this may have prevented polymerization beyond disulfuric acid and its anion.

Phosphoric Acids

For the phosphoric acid system less is known, but we can represent this system as follows

$$\begin{aligned} H_3PO_4 + H_3PO_4 &\rightleftarrows H^+ \cdot H_3PO_4 + H_2PO_4^- \\ &+ \\ &HPO_3 \\ &\Downarrow \\ &H_3P_2O_7^- \\ &+ \\ &HPO_3 \\ &\Downarrow \\ &H_4P_3O_{10}^- \\ &+ \\ &HPO_3 \\ &\Downarrow \\ &\text{polymer} \end{aligned} \qquad (7)$$

where metaphosphoric acid is considered the diphosphate ion acceptor.

A plot of the acidity function H_0 (to be defined later) from Temkin (*16*) shows a maximum at 80 mole per cent of P_2O_5 corresponding to $H_4P_2O_7$ and the decrease in acidity might be attributed to the formation of tripolyphosphoric acid (*17*).

Hydrocyanic Acid

Attention is called to HCN, another solvent which is also highly hydrogen-bonded, tends to polymerize,

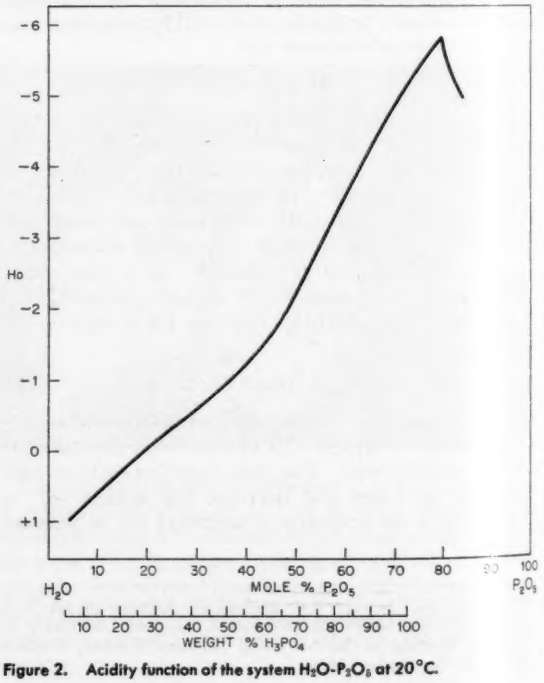


Figure 2. Acidity function of the system H_2O-P_2O_5 at 20°C.

has a high dielectric constant (ϵ = 123 at 16°C), and an ion product of 2×10^{-19} for $(H^+ \cdot HCN)(CN^-)$ at 12°C. HCN is an excellent solvent for most organic compounds, and ionic mobilities are several times greater than the values for the corresponding ions in water (*18*).

$$\begin{array}{c} HCN + HCN \rightleftarrows H^+ \cdot HCN + CN^- \\ + \\ CuCN \\ \Downarrow\Uparrow \\ Cu(CN)_2^- \end{array} \qquad (8)$$

Little is known about the solubility of the covalent cyanides in liquid HCN.

General Acidity Scale Problems

I should now like to discuss the theoretical and practical limitations of a general scale of acidity. For dilute solutions of proton acids in pure and relatively basic solvents, of not too low dielectric constant, we have

$$A_x + S \rightleftarrows SH^+ + B_x^- \qquad (9)$$

for the double acid-base reaction, and this equilibrium constant can be determined by at least four experimental methods: conductance, emf, spectrophotometry and solubility.

The resulting equilibrium constants are a measure of the relative acid strength of the acid A_x in the solvent S. In each solvent the standard acid is the solvated proton and the results in one medium are not comparable to those in another (*19*).

The exhibition of the acid property is the transfer of the proton from the acid to the base and not the dissociation of the acid-base complex into separate ions. When the acid A_1 reacts with the base B_1 the primary reaction is

$$A_1 + B_2 \rightleftarrows B_1A_2 \qquad (10)$$

and in an inert (aprotic) solvent of low dielectric constant $B_1^- A_2^+$ will not appreciably dissociate but may even associate to form dimers or higher polymers. The proton transfer may not be complete, and the complex may not be wholly ionic. In addition A_1 and B_2 may not represent a single species but may involve ionic or other associated species.

M. M. Davis and her co-workers (*20*) have carried out systematic studies of acid-base reactions, employing spectrophotometry in the visible region. The reaction studied is given by equation (10) where the association constant is a measure of the acid strength. This is analogous to the reactions of the Lewis acids where a proton may not be involved. However, AB may not be the only complex, as spectrophotometric studies show that more than one complex often results when the concentration of base is increased. For example, where A is the yellow acid bromophthalein magenta E, and the base 1,3-diphenylguanidine the primary change gives a magenta color, but on further addition of base the color is blue. These and other color changes may be explained in terms of complexes involving hydrogen bonds. The advantage of using indicator acids with absorption bands in the visible is that one can work in very dilute soutions, but infrared spectroscopy is applicable to a wider range of acidity. Barrow and Yerger (*21*) have investigated the extent of acid-base reactions by infrared spectroscopy in the solvents carbon tetrachloride (ϵ = 2) and chloroform (ϵ = 5). These studies show that the association between ion pairs is a specific interaction leading to hydrogen-bonded structures. The results in chloroform indicate a relatively strong interaction of the ion with the solvent. It is concluded that the role of each solvent cannot be understood in terms of the dielectric constant alone. These and additional studies in benzene (ϵ = 2) acetic acid (ϵ = 6), and other low-dielectric-constant solvents make it evident that quantitative values in any of these solvents must be preceded by a thoroughgoing study of molecular structure and the species involved in acid-base reactions.

The equilibrium constant just given is no longer a measure of the acid strength when the medium is changed. In terms of the formal definition of an acid

$$A \rightleftarrows B + H^+ \qquad (11)$$

the acidity constant is

$$K_{\text{acidity}} = a_{H^+} \frac{C_B}{C_A} \qquad (12)$$

where C_B and C_A refer to the acid and base involved, irrespective of their solvation in the solution. a_{H^+} represents what Brønsted called the absolute activity of the hydrion. If one had a series of solutions in which the ratio $C_B/C_A = 1$ or any other ratio and could measure the a_{H^+} the problem would be solved. The difficulty, which was pointed out long ago by P. B. Taylor of the University of Pennsylvania (1926), is that one cannot measure ionic free energies but only products and quotients. Basically the problem is the same as that involved in the standardization of the *p*H scale for aqueous solutions (*22*). Originally the *p*H scale was supposed to refer to concentration of the hydrogen ion, and it was suggested that the scale be replaced by a p_aH referring to the activity of the hydrogen ion. Strictly speaking neither concentration nor activity is ever measured on a thermodynamic basis and the lack of clarity in definitions and assumptions in attempting to measure either concentration or activity of hydrogen ion in aqueous solutions has led to a good deal of confusion. After all, one cannot measure a quantity any better than one can define it.

Since the thermodynamic constant for each particular acid is

$$K_{\text{activity}} = a_{H^+} \frac{a_B}{a_A} \qquad (13)$$

and

$$K_{\text{acidity}} = K_{\text{activity}} \frac{f_A}{f_B} \qquad (14)$$

variations in the acidity constants on changing from one medium to another are determined by the ratio of the absolute activity coefficients. The magnitude of this change will vary with the charge type of the acid. For positively charged acids, calculation shows that K_{acidity} would be expected to increase with decreasing dielectric constant while for uncharged or negatively charged acids K_{acidity} decreases with decreasing dielectric constant.

The quantities involved in $K_{acidity}$, namely, the absolute activity of the proton and the stoichiometric concentrations of A and B, are comparable for different acids and different solvents whereas the activities a_A and a_B can be compared for the same acid in different media but not for different acids in the same medium (*23*). A general measure of acid strength would be possible if a particular state could be found as an ideal reference state. For example, one might choose the vapor state and at some low pressure the activities of A and B would be equal to the concentration and the acid strength would be the acidity in an attenuated vapor at equal concentration of A and B. Practically the fact that two differentially charged species are involved in the acid-base equilibrium precludes this solution.

A less general solution can be found by assuming the activities of A and B become equal to their stoichiometric concentrations in ideal dilute aqueous solution. Hammett and Deyrup propose an acidity function (*24*)

$$H = -\log\left(a_{H^+}\frac{f_B}{f_A}\right) \qquad (15)$$

which yields

$$H = \log\frac{c_B}{c_A} - \log K_A \qquad (16)$$

This equation should be applicable to solvents of high dielectric constant but inapplicable elsewhere. The acidity function becomes equal to *p*H for dilute aqueous solutions. If B is an indicator base, c_B/c_A can be determined spectrophotometrically and K_a can be determined in water or related to K_a for an indicator of the same charge type in water by a stepwise procedure.

The assumption is made that H is independent of the nature of the base and evidence has accumulated in favor of this assumption where B is an uncharged base. This means the ratio f_B/f_A has the same value for all bases. When the base is negatively charged, the acid has a zero charge and these are simpler cases than for bases of other charges, for although the electrostatic contributions may cancel, the individual nature of the ions will be more important. For uncharged bases

$$H_0 = \log\frac{C_B}{C_A} - \log K_A \qquad (17)$$

Friedel-Crafts Reactions

The idea of ion acceptors can also be applied to reactions where a proton acceptor is not necessarily involved (*7*); for example, titanium tetrachloride which shows no measurable conductance in dry benzene or carbon tetrachloride, shows a marked maximum in the specific conductance curve in methylene chloride or methyl chloride (*25*). A plausible mechanism is a small self ionization of the titanium tetrachloride and the

$$TiCl_4 + TiCl_4 \rightleftarrows TiCl_3^+TiCl_5^- \rightleftarrows TiCl_3^+ + TiCl_5^- \qquad (18)$$

$$TiCl_4^- + RCl \rightleftarrows R^+ + TiCl_6^= \qquad (19)$$

alkyl chloride, followed by the displacement of the reaction to the right by formation of the stable anion $TiCl_6^=$, thereby increasing the concentration of both cations.

For aluminum bromide in methyl bromide the correct interpretation seems to be

$$4AlBr_3 \rightleftarrows Al_2Br_5^+ + Al_2Br_7^- \qquad (20)$$

$$Al_2Br_7^- + RBr \rightleftarrows R^+ + Al_2Br_8^= \qquad (21)$$

Aluminum bromide can be regarded as the catalyst, for the formation of the anion $Al_2Br_8^=$ increases the concentration of the carbonium ion and the rate of subsequent reaction. In the alkylation of benzene with paraffins a proton source is necessary and the mechanism may be the same as equations (3) and (2) and the halide acceptor is called a co-catalyst.

Acknowledgment

The research program upon which this paper is based was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is hereby made to the donors.

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Notes on Qualitative Analysis

EDITOR'S NOTE: The following papers have been collected over a period of months. A similar collection has appeared in previous August issues (J. CHEM. EDUC., **35**, 401 (1958) and **36**, 379 (1959)). It is the Editor's hope that collection into one place will prove more attractive to readers than the more frequently used editorial procedure of scattering items such as these through the pages of several issues. We apologize to authors who thus have had to wait to see their work in print.

We commend to readers' attention the fact that several of these represent the solution problems given to freshman students in qualitative analysis courses. We hope that publication in these pages can stimulate just such activity. If readers merely incorporate these ideas into their own laboratory instructions, our battle is only half won. If, beyond that, these ideas suggest to the readers that they use their own ingenuity in similar fashion, we are gratified.

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Semimicro Analysis of Alloys Containing Zirconium

Until recently methods of analyzing alloys in college qualitative analysis courses have been for the most part limited to the detection of the so-called common metals. But with the introduction of various other metals in alloys, in order to give them valuable properties, it now has become important to include these metals in a qualitative analysis scheme. The chemical reactions of zirconium, one of the metals which has become especially important in the atomic energy field, are well known so that the student should have no difficulty in analyzing an alloy for this metal.

As in previous work (*1*, *2*) the object was to develop a semimicro method of qualitative analysis for zirconium within the framework of a scheme used for the common metals (*3*).

In the analysis of the metal ions zirconium appears in Group III (ammonium sulfide group) as a hydroxide with iron and titanium after their separation by sodium hydroxide from aluminum and vanadium (*1*, *3*). In our method the three insoluble hydroxides are dissolved in dilute hydrochloric acid and zirconium separated by precipitation with arsenic acid. Then the zirconium arsenate is dissolved in concentrated hydrochloric acid and alizarin red S added (*4*). A red color proves the presence of zirconium.

The analysis of an alloy, to be of any value, should give at least an estimation of the amount of the metals. This is accomplished for zirconium by determining the number of drops (actually a titration) of a sodium fluoride solution, standardized in terms of the amount of zirconium, necessary to change from the red zirconium alizarinate to the yellow of the alizarin red S in hydrochloric acid. This color change results due to the formation of the zirconium fluoride complexion ZnF_6^{--}, thus liberating alizarin red S. An unusual result was obtained in that with low concentrations of zirconium the addition of alizarin red S did not give a red color. However if a little more arsenic acid is added, the red color appears. It was reasoned that in the concentrated hydrochloric acid the zirconium was present as some complex, possibly zirconium chloride complex ion, and therefore there was too little zirconium or zironyl ion (ZnO^{++}) to react with the alizarin red S. In some unknown manner the arsenic acid liberates zirconium ion from the complex. Analysis of various combinations of aluminum, iron (III), and titanium (IV) ions equal to 25 mg with 1 mg of zirconium ion showed that all the zirconium ion could be determined.

The method was carried out on alloys (25 mg sample) containing metals of other groups including antimony and tin which, in the nitric acid usually used to dissolve alloys (*5*), form precipitates of acids that tend to adsorb other metal ions (*6*). It was found that when the alloy contained as much as 20 per cent antimony (5 mg), at least 1 mg of zirconium was adsorbed by the antimonic acid. With less antimony in the alloy less zirconium was lost. Tin did not act the same way. The zirconium in the antimonic acid was easily determined by dissolving the latter in concentrated hydrochloric acid and carrying on the analysis. Alloys which did not contain antimony gave practically complete recovery of zirconium. The method is directly applicable to alloys having 0.4–10% zirconium and higher if an aliquot is taken.

The Experiment

Twenty-five milligrams of the alloy, preferably in small pieces, are heated with 1 ml of 7.5 *M* HNO_3 according to a standard method (*5*). Group II (copper and tin group) and Group III (ammonium sulfide group) are separated as sulfides using thioacetamide (*7*). Following a standard method (*1*, *8*) in Group III, the precipitate consisting of possible iron(III), titanium(IV) and zirconium hydroxides is dissolved in 2 ml of 3 *M* HCl. Then 3 drops of 0.1 *M* H_3AsO_4 are added and heated in a boiling water bath for one minute. The mixture is centrifuged, the centrifugate tested for complete precipitation, and the residue washed twice with distilled water. The precipitate is dissolved in 1 ml of conc. HCl, 1 drop of 0.05% water solution of alizarin red S (sulfate free) is added, followed by 2 drops of the arsenic acid. A red color proves the presence of zirconium ion. The amount of zirconium is determined by counting the number of drops of a 0.01 *M* NaF solution (kept in a polyethylene bottle and dropper to avoid action on glass) necessary to change the red color to yellow. The NaF solution should be standardized against known

amounts of zirconium ion under the same conditions as the determination and a curve drawn.

If a precipitate results from the initial treatment of the alloy with dilute HNO_3 (*5*) and antimony is found, a new sample of the alloy should be treated. The precipitate is washed twice with distilled water, dissolved in 1 ml of conc. HCl, and the above analysis for the amount of zirconium carried out.

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(8) Curtman, *op. cit.*, p. 274.

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A Study of Various Methods for the Analysis for Group III Cations

Many methods have been devised for the qualitative analysis of group III cations, but no one method has been shown to be superior to the other. Tenbusch and Brewer (*4*) surveyed procedures in various texts and outlined six different methods. Two of these are widely used. The first consists in separating group III into two divisions by the addition of a strong base (sodium or potassium hydroxide) and an oxidant (sodium peroxide or hydrogen peroxide). Iron, cobalt, nickel, and manganese are precipitated as insoluble, hydrous oxides while aluminum, chromium, and zinc, being amphoteric, go into solution as anions.

The other method uses ammonium hydroxide to separate iron, aluminum, and chromium as hydrous oxides from cobalt, nickel, manganese, and zinc which remain in solution. Neither method is entirely satisfactory since various ions are carried down in the gelatinous precipitates. Manganese is especially troublesome in the second method; about half is precipitated along with the hydrous oxides while the remainder stays in solution with the complex ammines. Curtman (*1*) and Welcher and Hahn (*6*) remove manganese first by precipitation of manganese dioxide from nitric acid solution; then they use ammonium hydroxide to separate the two divisions.

A method proposed by Kolthoff, Stenger, and Moskovitz (*2*) and studied later by Lehrman and Kramer (*3*) and Tomsicek and Carney (*5*) uses ammonium benzoate as precipitant in weakly acid solution. Iron, aluminum, chromium, and titanium are precipitated as insoluble, basic benzoates while manganese, cobalt, nickel, and zinc remain in solution.

Evaluation

The effectiveness of these three methods was studied using radioactive tracers, cobalt-60, zinc-65, and chromium-51. The following procedure was employed: Solutions containing 10 mg each of the group III ions (including titanium) and suitable tracer were precipitated or separated in an appropriate manner. The degree of contamination or coprecipitation was determined by measuring the gamma activity of the precipitate or solution using a well-type scintillation counter. In some samples a complete analysis was made to check the separation and identification of nontracer elements. Manganese was determined colorimetrically by oxidation to the permanganate.

Method I consisted in precipitating the hydrous oxides of iron, nickel, cobalt, manganese, and titanium using 2*M* sodium hydroxide and hydrogen peroxide (or sodium peroxide), leaving aluminum, chromium, and zinc in solution.

Method II consisted in precipitating the hydrous oxides of aluminum, chromium, iron, and titanium with 6*M* ammonium hydroxide leaving cobalt, nickel, manganese, and zinc in solution.

Method III consisted in precipitating the basic benzoates of aluminum, chromium, iron, and titanium by the addition of ammonium benzoate to a dilute, acetic acid solution (*5*). Cobalt, nickel, manganese, and zinc remain unprecipitated in the weakly acid solution.

Results are summarized in Table 1.

Table 1. Comparison of Methods for Separating Group III Cations

	Method	Per cent precipitated— Chromium	Cobalt	Manganese	Zinc
I	Sodium hydroxide + hydrogen peroxide	48.6	97.3	98.0	23.5
Ia	Sodium hydroxide + sodium peroxide	41.0	98.6	98.0	27.4
II	Ammonium hydroxide	86.7	11.5	50.0	5.8
III	Ammonium benzoate	88.2	5.8	5.0	4.2

After comparing the various methods, the following conclusions were drawn:

The best method for separating group III into two divisions consists in precipitating the basic benzoates of aluminum, chromium, iron, and titanium from hot, weakly acid solution. About five per cent of the division B cations, cobalt, nickel, manganese, and zinc, remain in the precipitate. One disadvantage of this method arises from the fact that crystals of benzoic

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acid are precipitated when the solution is allowed to cool. This does not cause any difficulties, however, and it does not interfere in the subsequent analyses. A procedure for this method is given later in this paper.

The major weakness of the ammonium hydroxide separation lies in the fact that manganese is distributed between divisions A and B. The degree of contamination depends upon the length of exposure to the air after the addition of ammonium hydroxide and upon what other cations are present.

The addition of hydroxylamine hydrochloride will inhibit the precipitation of manganese dioxide from ammoniacal solution but in the presence of ferric ions, there is still extensive coprecipitation. Separations from cobalt and zinc are not so good as in the basic benzoate method.

Poorest separations are attained by the use of sodium hydroxide along with an oxidant. Hydrogen peroxide is preferred over sodium peroxide as oxidant, since it is less hazardous and more convenient to use. About one quarter of the zinc and almost half of the chromium is lost by coprecipitation in this method.

In light of these studies the basic benzoate method is recommended for the separation of group III ions. The following procedure is a modification of the method of Tomsicek and Carney (*5*) for semimicro work.

(1) Take 1 or 2 ml of the unknown solution (groups I and II absent), acidify with 6 *M* hydrochloric acid; then add about 5 drops in excess. Add about 5 drops of ethyl alcohol, or formaldehyde; then heat and boil about 3 min. to reduce permanganate and dichromate ions.

(2) Add 6 *M* ammonium hydroxide dropwise, with stirring, until a permanent precipitate is formed, or until the solution is just basic. Add 1 ml of 6 *M* acetic acid and 2 ml of 1 *M* ammonium benzoate. Heat in a boiling water bath with occasional stirring, about 10 min. Centrifuge while hot and decant the supernate to a clean tube.

(3) Test for completeness of precipitation by adding 10 drops of 1 *M* ammonium benzoate to the supernate and heating again in the water bath for 5 min. Centrifuge and combine any precipitate with that from step (2). Save the supernate to analyze for Mn^{++}, Co^{++}, Ni^{++}, Zn^{++}.

(4) Wash the residue with 1 ml of 1 *M* potassium nitrate plus 2 ml of water. Stir, heat to boiling, centrifuge, and combine the washings with the supernate from step (3). Repeat this step a second time.

The residue is dissolved in 2–3 ml of hot, 6 *M* hydrochloric acid, then analyzed for Fe^{+3}, Ti^{+4}, Al^{+3}, and Cr^{+3}.

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Qualitative Analysis in a Soviet University

The study of a textbook,[1] a laboratory manual,[2] and a problem book,[3] published by the University of Kharkov, gives valuable information about the teaching of qualitative analysis in this university and generally in the universities of the Soviet Union.

The time assigned for the qualitative analysis laboratory is 180 hours. The cations studied in this period are silver, lead, mercury(I), bismuth, copper, cadmium, mercury(II), arsenic(III), arsenic(V), tin(II), tin(IV), antimony(III), antimony(V), nickel, cobalt, aluminum, chromium, iron(II), iron(III), manganese, zinc, barium, strontium, calcium, magnesium, potassium, sodium, ammonium, litbium, rubidium, and cesium. The anions studied are borates (BO_2^-, BO_3^{-3}, and $B_4O_7^{-2}$), carbonate, acetate, oxalate, tartrate, cyanide, thiocyanate, hexacyanoferrate(II), hexacyanoferrate(III), silicate, fluosilicate, nitrite, nitrate, phosphate, arsenite, arsenate, sulfide, sulfite, thiosulfate, sulfate, chromate, dichromate, fluoride, chloride, chlorite, hypochlorite, chlorate, bromide, iodide, and iodate.

All these cations and anions are required by the syllabus for analytical chemistry approved by the Ministry of Higher Education of the U.S.S.R. for chemistry majors in the universities in the year 1953. This syllabus was still in use at least as late as 1958.

The theoretical topics discussed in the text include all the material that is prescribed by the syllabus. They are dissolution and solutions, law of mass action, calculations with the help of the law of mass action, equilibrium in aqueous solutions of acids and bases, indicator theory, hydrolysis, complex compounds, oxidation-reduction reactions, solubility and solubility product, separation of the solid phase from a homogeneous

Presented before the Division of Chemical Education at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

[1] Komar', N. P., *Osnovy kachestvennogo khimicheskogo analiza.* ("The Principles of the Qualitative Chemical Analysis.") Kharkov. Izdatel'stvo Kharkovskogo Universiteta, 1955.

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[3] Komar', N. P., *Sbornik zadach, uprazhnenii i voprosov po kursu kachestvennogo analiza.* ("A Collection of Problems, Exercises, and Questions for the Course of Qualitative Analysis.") Kharkov. Izdatel'stvo Kharkovskogo Universiteta, 1954.

supersaturated solution, colloid solutions, precipitation of a slightly soluble substance in equilibrium conditions, washing and reprecipitation of precipitates, precipitation on a collector, elements of the chromatographic analysis, dissolution of compounds slightly soluble in water, extraction of substance soluble in water by solvents immiscible with water, buffer systems, organic reagents, and sensitivity of chemical reactions.

This theoretical material as covered in the textbook is on a high level and much of it would be covered in an advanced course in this country.

In the laboratory work twelve unknowns are included in this syllabus for qualitative analysis.

The material is divided into five units:

Unit one—two unknowns for group V ("group I" in America) cations. One of them contains a precipitate insoluble in water. The simple anions (sulfate, chloride, nitrate, and carbonate) should be discovered along with the cations in these unknowns and in all the following.

Unit two—one unknown for group IV cations, and one for the mixture of groups IV and V cations.

Unit three—one unknown for group III cations, and one for the mixture of the cations of groups III, IV, and V.

Unit four—one unknown for a mixture of cations of groups II and I, and one for a mixture of cations of groups III, II, and I in the presence of phosphate ion.

Unit five—two unknowns for anions.

Two general unknowns are given—one, an alloy, and another, a mixture of salts or a mineral.

Every unit is studied according to the following scheme:

Preliminary experiments, compiling a table of the reactions in all ions in the group, answering questions, and preparing an outline of the procedure.

An oral examination before receiving the unknown.

Analyzing an unknown and filling in a detailed report card.

The procedure of cation analysis recommended for these unknowns is rather classical. (Group precipitation by HCl, H_2S in acid and basic solutions, carbonates, etc.)

The preliminary experiments in the manual are described in such a way that the results are not given to the student. The semimicro method is used in the manual and apparently is now accepted by the majority of schools in the Soviet Union.

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A New Reagent for the Identification of Magnesium and Bismuth

Most of the qualitative textbooks used for undergraduate courses now have as one test the use of *p*-nitrobenzeneazoresorcinol, which forms a blue lake with $Mg(OH)_2$.

The author has discussed a series of new indicators formed by the condensation of phenols with pyromellitic acid dianhydride, PMDA.[1, 2, 3] Of these indicators one in particular, the brominated tetraresorcinol pyromellitein, forms a very highly colored crimson lake with $Mg(OH)_2$, which may be used to detect Mg^{++} in water solution to about 1 ppm as Mg^{++} in the absence of NH_4^+ salts.

A water solution of this indicator may be prepared easily by dissolving 1 g in a liter of water and adding a few drops of 0.1 *N* NaOH to aid solution. It has a light red color in basic solution changing to light orange around a *p*H of 2. The basic form is fluorescent under blue and the near ultraviolet light.

In the analysis of Group IV solutions, Ba^{++}, Sr^{++}, and Ca^{++} may be removed using $(NH_4)_2Co_3$. To a 1-ml sample of the filtrate in a semimicro test tube, one drop of the indicator should be added, and the solution made strongly basic with NaOH. A scarlet lake will precipitate even in the presence of carbonate.

For small amounts of Mg^{++}, the solution may be acidified with HCl and warmed to remove carbonate. This solution may then be made basic with NaOH and warmed to remove NH_3, after adding the drop of indicator. For small amounts, diluting the indicator gives a more pronounced change as the precipitate forms, since the lake is much brighter in color than the solution.

This indicator has been compared with *p*-nitrobenzeneazoresorcinol using the same solutions of Mg^{++}, and has proved to be more sensitive. It has been found that the precipitates formed retain their color indefinitely, while those with *p*-nitrobenzeneazoresorcinol turn brown on standing.

Bismuth

The same indicator forms a vivid scarlet color with $Bi(OH)_3$ and does not give a colored precipitate with Cu^{++} or Cd^{++} in NH_3 solutions. $Pb(OH)_2$ gives a pink color which will dissolve in NaOH, while the scarlet color of the bismuth lake is not removed by NaOH.

In Group IIA, the lead may be removed as sulfate, as in conventional procedures. After dilution, one drop of the indicator reagent should be added before making the solution strongly basic with NH_3. A scarlet color indicates Bi^{3+}. A light pink precipitate could be due to lead, and will dissolve easily in NaOH.

Assistance in this project has been received from the National Institutes of Health (P.H.S. Grant 5736). The PMDA used was contributed by E. I. du Pont de Nemours & Co., Inc.

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[2] *Op. cit.* **22,** 221 (1960).
[3] *Ibid.*

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Improved Confirmatory Test for Chromium

A test in the qualitative analysis scheme which has always given trouble is the confirmatory test for chromium. This test involves production of CrO_5 by oxidation with hydrogen peroxide in nitric acid. The instability of the CrO_5 in nitric acid is circumvented somewhat by extracting the blue CrO_5 with ethyl ether, in which its stability is a little greater.

The new test has been successfully used in routine qualitative analysis work by freshman students. The modified test also removes the necessity of having ethyl ether in the freshman laboratory with the accompanying hazard of fire and explosion. The work of the students consisted of investigating various related organic solvents as possible substitutes for ethyl ether. Ethylene glycol mono-butyl ether was found to be a much better solvent than ethyl ether. Conditions and concentrations were varied until a practical test was devised.

The test is performed as follows. After standard qualitative analysis procedure[1] has yielded a precipitate suspected to be barium chromate, 3 drops of 3 *M* HNO_3 (stir), 10 drops of water, 10 drops of ethylene glycol mono-butyl ether, and 1 drop of H_2O_2 are added in that order. The blue color indicating CrO_5 is quite intense and lasts about 20 minutes when the test is run on the precipitate obtained from 6 drops of an Al-Ni group test solution containing all ions at 0.1 *M* concentration. The blue color which results when ethyl ether is used under similar conditions lasts only a matter of seconds and sometimes does not appear if the concentrations of HNO_3 and H_2O_2 are too great or the temperature is too high.

Students have found that they are able to detect very low concentrations of dichromate ion using this method. At room temperature they have reported a positive test from a 0.00005 *M* solution of potassium dichromate at a *p*H of 7.

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A Non-Cyanide Separation of Copper from Cadmium

A procedure has been developed for the separation of copper from cadmium which is based upon the observation that thiocyanate ion will precipitate copper but not cadmium from an acidic solution.

To 1–2 ml of the ammoniacal solution remaining after the separation of bismuth, add 17 *F* $HC_2H_3O_2$ until the solution is distinctly acidic. Treat this solution with solid Na_2SO_3 (approximately 0.1 g), add 4–6 drops of 3 *F* NH_4CNS, mix thoroughly, and centrifuge. Formation of a white precipitate indicates the presence of copper in the sample. Test the supernatant liquid for completeness of precipitation by adding another drop of 3 *F* NH_4CNS. Decant the clear solution and pass in H_2S for 1 min. A yellow precipitate indicates the presence of cadmium.

In the above procedure, the acetic acid is added to decompose the Cu(II) and Cd ammines and to provide the hydrogen ion concentration necessary to liberate SO_2, which reduces Cu^{++} to Cu^{+}. The copper is then precipitated as white CuCNS. Mellor[1] states "cupric salts with potassium thiocyanate give black cupric thiocyanate, $Cu(CNS)_2$, which is slowly changed into white cuprous thiocyanate, CuCNS, or quickly on adding sulfurous acid." Under the conditions given here, the black Cu(II) salt has never been observed.

For the concentrations of cupric ion ordinarily present in qualitative analysis unknowns, the blue color of the cupric ammine complex is generally sufficient as a confirmatory test. Absence of a pronounced coloration, however, does not exclude the possibility of Cu^{++} being present. The precipitation of CuCNS therefore can be used as a confirmation of copper as well as a separation where it is present in small amounts.

[1] Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green, and Co., London, 1923, vol. III, p. 103.

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Separation of Mn and Zn from Co and Ni by Fractional Dissolution of Their Sulfides

Group III cations are frequently separated into two divisions by treating the solution with excess ammonium hydroxide. Iron, aluminum, chromium, and titanium (division A) are precipitated as hydrous oxides leaving in solution the divalent ions, manganese, zinc, cobalt, and nickel (division B). A better separation is attained if division A is precipitated as basic benzoates.[2,4]

Various methods have been proposed for the separation and analysis of division B ions. Tomsicek and Carney[4] separate manganese as manganese dioxide by the addition of potassium chlorate to a hot, concentrated nitric acid solution of the ions. This method is undesirable since it is time-consuming and hazardous.

McAlpine and Soule[3] separate the sulfides of manganese and zinc from cobalt and nickel using 1*M* HCl as solvent. Manganese is then separated from zinc by the addition of NaOH and bromine water. This method is not very satisfactory since cobalt and nickel sulfides dissolve partially in 1*M* HCl. Upon treatment with NaOH and bromine water a black precipitate of $Co(OH)_3$ and $Ni(OH)_3$ forms, and this is frequently confused with manganese dioxide. Zinc is frequently carried down in the manganese dioxide precipitate, thus decreasing the sensitivity of the final confirmatory test.

A study was made of the solubilities of the sulfides of manganese, zinc, nickel, and cobalt in various acids. The following procedure was used: A solution containing 10 mg each of Mn(II), Zn(II), Co(II), and Ni(II) ions was made basic with NH_4OH. Two ml of 1*M* thioacetamide was added and the mixture heated in a boiling water bath until precipitation was complete. Solubilities were determined by adding known amounts of appropriate radioactive tracers before precipitation, then determining the activities of the solutions or precipitates after treatment with appropriate acids. The results are given in Table 1.

A consideration of these data suggested a new method of separation. The four sulfides, MnS, ZnS, CoS, and NiS, are treated first with 1 *M* acetic acid. Manganous sulfide dissolves completely, leaving ZnS, CoS, and NiS. The acetic acid solution is boiled to remove H_2S, HNO_3 is added, and manganese is identified by oxidation to the permanganate using sodium bismuthate or lead dioxide.

Table 1. Solubilities of Sulfides in Various Acids at Room Temperature

Acid and concentration	Per cent of sulfide dissolved		
	CoS	ZnS	MnS
1*M* HCl	28.0	61.0	100
1*M* HCl (ice cold)	17.4	47.5	100
2*M* HCl	28.2	84.4	100
1*M* $HC_2H_3O_2$	1.7	0.3	100
6*M* $HC_2H_3O_2$	68.4	...	100
3*M* H_2SO_4	74.7	...	100
1*M* $HClO_4$	30.4	64.3	100

The remaining sulfides are treated with cold, 2*M* HCl, which dissolves zinc sulfide and small amounts of cobalt and nickel sulfides. Zinc is identified by precipitation of the sulfide from a citrate buffer at a *p*H of 2. The residue of nickel and cobalt sulfide is dissolved in acid; then nickel is detected by precipitation with dimethylglyoxime and cobalt by the formation of its blue thiocyanate complex. A detailed procedure follows.

(*a*) *Separation of division A and B.*

Use NH_4OH or basic benzoate method.[2,3]

(*b*) *Separation of manganese.*

Precipitate the sulfides from ammoniacal solution using H_2S or thioacetamide. Let stand about 15 min. to age; then centrifuge and discard supernate. Add 3 ml of cool (room temperature), 1*M* acetic acid. Stir vigorously, centrifuge and decant the supernate to a clean tube. Heat and boil for about 2 min. to expel H_2S; then add 2 ml of 6*M* HNO_3 and solid sodium bismuthate. Permanganate color identifies Mn.

(*c*) *Separation of zinc.*

Treat the residue from step (*b*) with 2 ml of cool (room temperature) 2*M* HCl. Stir vigorously, centrifuge *immediately*, and decant the supernate to a clean tube. Add 5 ml of 1*M* sodium citrate and treat with H_2S. A white-gray precipitate of ZnS identifies Zn.

(*d*) *Identification of cobalt and nickel*

Add 2 ml of 6*M* HCl and 1 ml of 6*M* HNO_3 to the residue from step (*c*). Heat and boil to dissolve, then dilute with 2 ml of water. Divide into two portions.

Test one portion for nickel by making ammoniacal and adding dimethylglyoxime. Test the other portion for cobalt by adding 3 ml of acetone saturated with KSCN. A blue color identifies cobalt.

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Precipitation of the Hydrogen Sulfide Group of Ion using Thioacetamide

In the current texts in qualitative analysis there is considerable variation in the procedures recommended for precipitation of the hydrogen sulfide group using thioacetamide as the source of hydrogen sulfide. Hogness and Johnson[1] substitute thioacetamide for H_2S gas without change in the concentration of the H^+ ion. Barber and Taylor[2] begin the precipitation at the classical H^+ ion concentration of 0.2–0.3*M*, and then dilute the solution to 0.1*M* H^+ ion concentration for complete precipitation of PbS, CdS, and SnS. King[3] uses essentially the same procedure as Barber and Taylor. Nordmann,[4] after an initial precipitation at 0.3*M* H^+ ion, dilutes to about 0.15*M* H^+ ion concentration. Moeller[5] recommends precipitation of the group from a solution initially 2*M* in HCl and states that hydrolysis of the thioacetamide to acetate reduces the acidity of the solution to the customary concentration of 0.3*M* H^+ ion.

Swift and Butler[6] find that the hydrolysis of thioacetamide to hydrogen sulfide and acetamide is first order with respect to H^+ ion concentration and to thioacetamide concentration. Further, the acetamide is hydrolyzed to acetate so slowly that within the time required for the precipitation and separation of the hydrogen sulfide group the use of thioacetamide does not cause difficulty in the adjustment or control of the *p*H. With respect to the practice of beginning the precipitation in a small volume of solution of high acidity and then diluting the solution to obtain quantitative precipitation of the lead and cadmium these authors state:

> A similar dilution of the thioacetamide solution would leave a solution which is not saturated with hydrogen sulfide and from which, unless care is observed in any subsequent heating, hydrogen sulfide can be expelled more rapidly than it is produced by hydrolysis. Thus lead sulfide precipitates produced by such a dilution with cold water have dissolved when the solution was subsequently heated to boiling even though an excess of thioacetamide was present. Finally, in an attempt to adapt thioacetamide to the precipitation of the hydrogen sulfide group of elements, the precipitation of lead was found to be incomplete under conditions which had been satisfactory with gaseous hydrogen sulfide.

The escape of hydrogen sulfide from the hot solution appears to be a major difficulty in obtaining complete precipitation of the hydrogen sulfide group. At the temperature required for rapid hydrolysis of thioacetamide the H_2S gas is lost nearly as fast as it is formed; hence, the concentration never gets high enough for complete precipitation of the sulfides of lead and cadmium.

The loss of hydrogen sulfide gas during the hydrolysis of the thioacetamide can be prevented by capping the reaction vessel with a balloon. After the hydrolysis is complete the trapped hydrogen sulfide can be redissolved by cooling and agitating the capped reaction vessel. The larger amount of H_2S retained in the solution during hydrolysis, together with that redissolved from the balloon, gives complete precipitation of the hydrogen sulfide group from a solution 0.3*M* in H^+ ion.

For precipitation on a semimicro scale a 13- × 100-mm test tube with a volume of about 10 ml is a satisfactory reaction vessel. The penny balloons from the toy counter of a variety store fit snugly over the lip. If the test tube is half full of liquid there is only 5 ml of air in the system. If 1 millimole of thioacetamide is present, its hydrolysis gives 20 ml of H_2S gas. Thus the gas in the capped system is rich in H_2S and the solution can be saturated with the gas by cooling and agitating the tube.

Thioacetamide is much more readily oxidized than is hydrogen sulfide gas. Hydrogen peroxide rapidly oxidizes thioacetamide to free sulfur. Roughly, one drop of 3% H_2O_2 solution oxidizes one drop of 1*M* thioacetamide. Hence, if hydrogen peroxide is used to oxidize Sn(II) to Sn(IV) prior to precipitation, the quantity added should be kept to a minimum. On the positive side, thioacetamide reduces As(V) to As(III) and As_2S_3 is precipitated rapidly. When thioacetamide is used as the source of H_2S the arsenic is precipitated without using NH_4I as a reducing agent.

Under the conditions usually encountered in student unknowns the following procedure gives complete precipitation of the hydrogen sulfide group on a single treatment with thioacetamide. An unusually high concentration of chloride ion can prevent the precipitation of cadmium. If a large amount of oxidizing agent is present the thioacetamide may be destroyed.

Adjust the volume of the unknown solution to 2 to 3 ml. Neutralize the solution, make it just acidic with HCl, and then add 5 drops of 6*M* HCl in excess. Add two drops of 3% H_2O_2 solution and heat the solution to boiling to oxidize any Sn(II) to Sn(IV). Add 1 ml of 1 *M* thioacetamide solution and dilute to 5 ml. Transfer the solution to 13- × 100-mm test tube.

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[1] Hogness, T. R., and Johnson, W. C., "Qualitative Analysis and Chemical Equilibrium," 4th ed., Henry Holt and Company, New York, 1954, p. 419.

[2] Barber, H. H., and Taylor, T. I., "Semimicro Qualitative Analysis," Revised ed., Harper and Brothers, New York, 1953, p. 173.

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Cap the test tube with a deflated balloon. Heat the tube in a bath of boiling water for 10 min. (Slightly less air is trapped in the system if the tube is heated for about a minute, capped, and then returned to the boiling water for ten minutes.) Without removing the balloon, cool the test tube under the tap or in a beaker of cold water. For about a minute, agitate the cold test tube as vigorously as possible without getting the solution up into the balloon. Remove the balloon, centrifuge, and decant the supernatant liquid into a second 13- × 100-mm test tube. Test the acidity of the solution with methyl violet paper, and, if necessary, adjust the H^+ ion concentration to the original value of $0.3M$. To test for complete precipitation, add 5 drops of $1M$ thioacetamide, cap the test tube with a balloon, and heat it for 10 min. in a bath of boiling water. Cool and agitate the tube to redissolve trapped H_2S. If any additional precipitate is formed, pour the suspension into the test tube containing the previously precipitated sulfides and centrifuge again. Continue to test for completeness of precipitation until no further precipitation occurs.

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The Detection of Acetate Ions in Qualitative Analysis

Although several tests for the acetate ion are currently in use, none of these is very reliable. The characteristic odor, either of the acid itself or its ester (after addition of H_2SO_4 and amyl or ethyl alcohol), is often obscure. The basic ferric acetate test is not reliable since hydrolysis of the ferric chloride may occur. Many anions interfere with the simple litmus paper test for volatilized acetic acid.

A reliable test for acetate has been developed which is based upon the fact that acetate ion pyrolyzes with sodium hydroxide to form sodium carbonate. The pyrolyzed unknown is acidified, and effervescence indicates the presence of acetate in the original sample. Other anions, such as $CO_3^=$, $S_2O_3^=$, $C_2O_4^=$, $C_4H_4O_6^=$ and the cyanides, give a similar test. These are removed by precipitation with $Ca(NO_3)_2$-$AgNO_3$ solution. The following procedure is recommended:

Procedure. To 10–15 drops of unknown, add $3N$ NaOH until slightly basic. Add $Ca(NO_3)$-$AgNO_3$ solution, centrifuge and discard the residue. Check the centrifugate for complete precipitation. Add sodium chloride solution to remove excess silver ion, and again centrifuge and discard the residue. Reduce the centrifugate volume to ten drops by evaporation, then transfer to a crucible and add ten drops $3N$ NaOH solution. Cover the crucible and heat gently to dryness (two minutes). Then heat strongly one additional minute. Let cool, then remove the cover and add a few drops $6N$ HCl. Effervescence identifies acetate. This test is sensitive to 5 mg of acetate ion.

[1] *Editor's Note:* This note was submitted by Professor Richard B. Hahn of Wayne State University who says, "Recently Mr. Berk and Mr. Hecker, students at Cass Technical High School, told me that they had developed a new test for acetate ion. I was impressed by their originality, enthusiasm and systematic investigation of the problem and urged their submission of this note to the JOURNAL OF CHEMICAL EDUCATION."

Notes on Thioacetamide

An annotated bibliography of over 80 references to the literature on the use of thioacetamide as a sulfide precipitant has been compiled by W. C. Broad and A. J. Barnard, Jr., of the J. T. Baker Chemical Company, Phillipsburg, N. J. It is available free on request.

The use of thioacetamide as a sulfide precipitant in place of gaseous H_2S has steadily gained popularity since first proposed in 1934. The hydrolysis of aqueous solutions is controlled simply by heating. The metal sulfide precipitates produced have physical characteristics which make them easily filterable. Thioacetamide is a practical reagent for about 20 metals.

Analysts, and especially teachers whose qualitative analysis classes use a sulfide separation scheme, will find this nine-page pamphlet a convenient first place to look for information.

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Textbook errors, 26

Solubility of Gold in Mercury

It is not surprising that many chemists have the erroneous impression that gold is rather soluble in liquid mercury. Of all the textbooks which have been examined,[2] only one explicitly states that the amalgamation process for gold recovery depends on the wetting of gold by mercury and not on the solubility of gold in mercury. The amalgamation process is now becoming obsolete, but when it is discussed, many authors either state or imply that it works because the gold dissolves in mercury.

A commercial application of the fact that gold does not dissolve in mercury is to be found in the "gold-adhesion" filter.[3] In this device a ring of gold alloy surrounds an aperture through which mercury passes. Floating contaminants (oxide scum, water, oils, etc.) are prevented from working down between the mercury and the sides of the container and out the aperture by the adhesion of mercury to the easily "wet" gold ring. (*12*). Purity approaching that of triple distilled mercury is claimed when this filtration is preceded by vigorous aeration.

At least two previous publications (*9*, *23*) have pointed out that textbook explanations of the gold amalgamation process have been misleading. However, continued promulgation of this error in the most recent texts would seem to justify repetition in THIS JOURNAL of the accurate solubility data.

These textbook discussions probably result from the statements about the gold amalgamation process in several of the more frequently consulted reference works. One of them states that "gold is miscible in mercury in all proportions." Similar statements are to be found in other treatises on inorganic chemistry and even in metallurgical reference works. The solubility figures given in one case (*7*) actually are values for the solubility of mercury in solid gold (*2*), not for gold in mercury!

The opacity of mercury suspensions (or solutions) of metals precludes an easy observation of homogeneity. This fact alone is probably the chief reason for the assumption that gold is soluble in mercury. Visual observation will disclose nothing about the homogeneity of the system. Several authors (*3*, *4*, *13*) have discussed the definition of solubility and particle size in relation to the problem of determining whether a given mercury-metal system is a saturated solution or a suspension of small metal particles in the mercury. Most investigations of metal-in-mercury solubility have used some sort of filtration process to separate the solution from suspended particles. Because of the variability of pore sizes for the different filtering media, it has been suggested that reported values for metal solubilities in mercury tend to be too high rather than too low.

As early as 1855 Henry (*8*) had noted that the solubility of gold in mercury was 0.14% and in 1878 Kasantseff (*10*) observed the gold content of saturated liquid amalgam was only 0.11, 0.126, and 0.65% at 0, 20, and 100°C, respectively. In 1903, Richards (*19*) made reference to three different amalgams of gold. The first is a saturated solution of gold in liquid mercury containing about 0.1% gold. His second amalgam is a solid gold mercuride. (Richards suggested the formula Au_3Hg_2. Later evidence would indicate that this second amalgam is probably a solid solution of mercury in Au_3Hg.) Richards' third form is "nuggets of gold superficially coated with and cemented together by the other two forms of amalgam."

Very careful determinations of the solubility of gold in mercury were made in Professor Sunier's laboratory at University of Rochester (*1*, *11*, *22*, *23*, *24*) and by Plaksin in Russia (*14*, *15*, *18*) about 30 years ago. More recently, Strachan and Harris (*21*) have studied the solubility of a large number of metals in mercury. The results of these studies are in agreement with the solubility values given above and indicate that gold should be considered only very slightly soluble in mercury.

Table 1. Selected Values of Low Temperature Solubility of Gold in Mercury

Temperature (°C)	Solubility (atom %)	Reference
0	0.11	(*10*)
6.96	0.1006	(*23*)
20.00	0.126	(*10*)
"Room"	0.128	(*21*)
20.00	0.1290	(*23*)
39.98	0.2045	(*23*)
60.32	0.3152	(*23*)
80.8	0.467	(*22*)
101.2	0.697	(*22*)

The accompanying table presents selected values of the low temperature solubility of gold in mercury. The gold-mercury phase diagram shown in the figure is drawn principally from data of Plaksin (*18*) except that the liquidus curve from 100 to 400°C is drawn from

Suggestions of material suitable for this column and guest columns suitable for publication directly are eagerly solicited. They should be sent with as many details as possible, and particularly with references to modern textbooks, to Karol J. Mysels, Department of Chemistry, University of Southern California, Los Angeles 7, California.

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[2] Since the purpose of this column is to prevent the spread and continuation of errors and not the evaluation of individual texts, the source of errors discussed will not be cited. To be presented, the error must occur in at least two independent standard books.

[3] Available from The Bethlehem Apparatus Company, Inc., Hellertown, Pa.

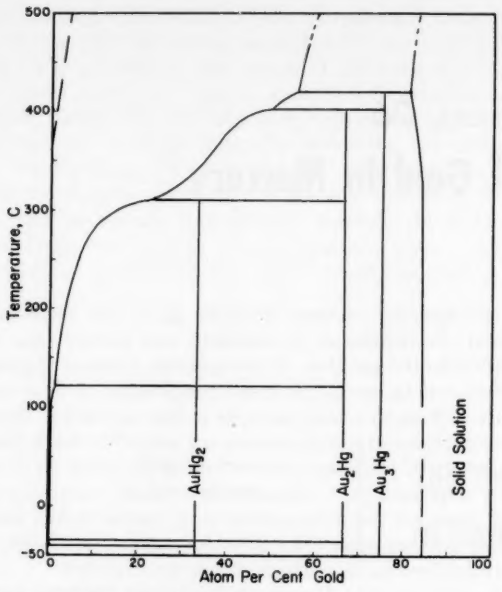

Figure 1. Gold-mercury phase diagram

Sunier's solubility data (*1*), and the solid solution of mercury in gold is drawn according to Day and Mathewson (*2*). The eutectic temperature is about 0.1° below the freezing point of mercury and corresponds to almost pure mercury. Polymorphic transformations of $AuHg_2$ are represented by horizontal lines at −36 and 122°. The dashed line in the upper left corner of the diagram has been sketched in to show the vaporization of mercury.

Perhaps these pages are an appropriate place to direct textbook authors' attention to Gmelin's statement: "Die Goldamalgamation ist ein komplizierter, noch nicht vollkommen geklärter Vorgang" (*6*). ("The amalgamation of gold is a complicated, and as yet incompletely explained process.") Mechanical mixing, chemical bonding, wetting, solution and alloying all enter into the process. The gold in the crushed ore is wet by the mercury and held on the amalgamating plate (Hudson (*9*) suggests a fly paper analogy); chemical reaction of gold with mercury then proceeds very slowly. Periodically, the amalgam is scraped from the plates, cleaned, and then squeezed through chamois skin or fine canvas to give cakes containing 40 to 50% gold (*5*). The mercury recovered from this operation is usually used over again in the mill, since chemically pure mercury is not as effective a wetting agent for gold as is that which contains small amounts of gold (*16*, *17*, *20*). The pressed amalgam is then retorted to distill off the mercury dissolved in (and chemically bound to) the gold. The ingots cast from the retorting residue usually contain more than 80% gold, perhaps 16% silver, and small amounts of base metals such as copper and iron (*5*, *19*).

The process outlined above works because gold does not dissolve in the mercury. If gold were soluble in mercury to any great extent, very little gold would be recovered from retorting the pressed amalgam.

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AIBS Translation Program

The American Institute of Biological Sciences is currently translating and publishing seven Russian research journals in biology. These journals are translated with support from the NSF, which is eager that such information be more widely distributed to biologists throughout the world. The journals currently being translated are: Doklady: Biological Sciences Section; Doklady: Botanical Sciences Section; Doklady: Biochemistry Section; Plant Physiology; Microbiology; Soviet Soil Science; and Entomological Review. Additional information pertaining to this program may be obtained by writing to the American Institute of Biological Sciences, 2000 P Street, N. W., Washington 6.

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Peter Shaw

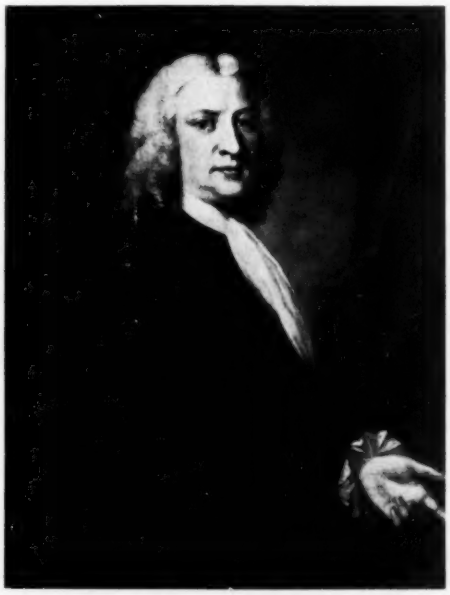
Peter Shaw was born in 1694, the youngest son of Robert Shaw, the Master of Lichfield Grammar School. Nothing of importance was heard about him until his emergence at the age of 29 as an author and competent Latin translator, when he published his version of John Quincy's lectures on pharmacy.[1] The book was dedicated to Joseph Collet who was responsible for the production of the *Pharmacopoeia* of 1721. This particular *Pharmacopoeia* was notable in that it considerably simplified the medicinal preparations in use at the time, and since Shaw was concerned about the neglect of pharmacy, it is more than likely that the dedication reflected his admiration for the work of Collet. Shaw was already styling himself M.D. although with, it appears, little justification. There is no doubt, however, that his approach to medicine was sound and scientific. He deplored the poor progress made in the science of healing: diagnosis without accompanying skill in pharmacy did not seem to him to be one of the attributes of a good doctor, and he was loud in his condemnation of all quacks, charlatans, and "mercenary mystics."

Translator and Author

In the same year he published a book on incurable diseases.[2] This work was significant in that it called for a true scientific approach to the study of medicine—"[t]hat way of reasoning," as he put it, "from Data to Quaesita which has done wonders in Philosophy, Astronomy and Mechanicks." The term incurable was, to him, only a relative one: in due course, with the proper approach, all diseases would be cured. "Physic," he said, "will tend to perfection as pharmacy flourishes."

Two years later he published an abridged account of the works of Robert Boyle[3] who had died in 1691. It is in this work that we first see clearly Shaw's belief in the potential value of chemistry to the arts and industry. Hermann Boerhaave had, in 1718, taken the chair of chemistry at Leyden and his inaugural address had clearly impressed Shaw who quoted from it liberally in the preface to the section on chemistry. Boerhaave, although not distinguished by his experimental researches, will be remembered for his clear recognition of chemistry as an independent science.

Shaw's enthusiasm for the scientific method of Boerhaave is reflected in his publishing in 1726, in conjunction with Ephraim Chambers, a book entitled, "A New Method of Chemistry" which was largely a collection of Boerhaave's chemical lectures. This was, in many ways, an unfortunate publication as we shall see. In 1724, an unauthorized text of these lectures, full of gross errors, had been published in Paris and had roused Boerhaave to a fury. Shaw and Chambers recognized the poor quality of this work and obtained copies of the lectures from Leyden students, endeavoring thereby to produce a collection of these lectures free from error. The book was well received in Great Britain, but although Shaw and Chambers gave full credit where it was rightly due, Boerhaave, understandably, remained furious.



(Courtesy the Royal College of Physicians and the National Portrait Gallery.)

Peter Shaw

During the next three years, Shaw published a number of important chemical works, including Stahl's "Fundamenta Chymiae," this also being based on students' lecture notes. Shaw apparently concurred in the phlogiston theory as did Boerhaave in many points, but it is interesting to note that Boerhaave experimentally contradicted the view that during calcination the so-called fire-stuff was taken up, thus causing an increase in weight. In one of his later works, Shaw's adherence to the older view shows that he was either unaware of, or that he did not agree with, Boerhaave's view. In spite of all this, Shaw's aim in publishing

[1] QUINCY, JOHN, "Praelectiones Pharmaceuticae; or a course of lectures in Pharmacy, Chymical and Galenical," published from his original manuscript, with a Preface by P. Shaw, M.D., London, 1743.

[2] SHAW, PETER, "A Treatise of Incurable Diseases," London, 1723.

[3] SHAW, PETER, "The Philosophical Works of the Honourable Robert Boyle, Esq.," London, 1725.

Stahl's work was not to support the phlogiston theory, but to advance scientific method generally.

Shaw, the Lecturer

Shaw now became interested in the production and use of a portable laboratory which would be suitable for prospectors, consulting chemists, and other gentlemen who might wish to study chemistry at home. To this end he joined with Francis Hauksbee who was the Librarian and Keeper of the Royal Society's Museum at Crane Court. In due course, an advertisement appeared stating that a "Portable Laboratory, ready fitted for Business may be had of Mr. Hauksbee in Crane-Court, Fleet-street London," and in 1731 a course of lectures was given by Shaw with experiments and demonstrations by Hauksbee. The charge for this course was five guineas, and the portable laboratory was on sale to interested subscribers. The lectures were apparently quite a success for they were repeated the following year and again at Scarborough in 1733. They were published by T. and T. Longman in Pater Noster Row in 1734 and were dedicated to Lord Lonsdale, the Lord Privy Seal, who found time to peruse the manuscript before publication. The lectures were designed, Shaw tells us, "to enlarge the Bounds of Chemistry by applying it to the Advancement of Natural Philosophy, the Illustration and Improvement of the known Arts and the Discovery of new ones." At the outset he made it clear that he regarded chemistry as, "a rational Art of dividing or resolving all the Bodies within our Power by means of all the Instruments we can procure: as well into integrant as constituent Parts; and joining these Parts together again; so as to discover the Principles, Relations and Changes of Bodies; make various Resolutions, Mixtures, and Compositions; find out the physical Causes of physical Effects; and hence improve the State of natural Knowledge and the Arts thereon depending."

The first lecture was accompanied by some eight experiments but Shaw was careful to point out, "that experiments are but insignificant Facts, unless they have a direct Use in Life." Succeeding lectures dealt with fire, air, earth, water, and solvents but after this preliminary treatment the subjects were largely concerned with industrial or possible industrial processes.

In the seventh lecture, given on fermentation processes, he suggests, albeit somewhat naïvely, that since the basis of winemaking is the fermentation of sugar, colorless, flavorless "wine" could be made in the Sugar Colonies. It would then be a simple matter to add color and flavor in the form of essential oils and so exactly to imitate sacks, sherries, ports, etc. Shaw was undoubtedly a little cynical about the ability of the palate to distinguish between real and artificial wines. He developed this theme in a later lecture, suggesting that in good years essences of crops such as hops should be made so that they could be used in lean years. He was, perhaps, a little uneasy about such suggestions; "... there would here be Danger of Fraud; because the Extracts of Gentian, Centaury, or other bitter stomachic Vegetables might be mixed with the Extract of Hops, so as not to be easily discovered." He eased his conscience a little by the suggestion that, after all, "... the Extract of Gentian is a wholesome Bitter."

The axioms and canons with which he ended this as well as other lectures, show that he was a clear and lucid thinker. Subsequent lectures dealt with such subjects as essential oils and salts, dyes and pigments, pharmaceutical chemistry, mineralogy, metallurgy, and pyrotechny.

The final lecture in the series was a masterly summing-up of the situation. He reviewed the possibilities of the introduction of new arts or trades in England with, perhaps, a slight overemphasis on the desirability of the production of commodities such as arracks and brandies, and stressed the need for improvements in many chemical trades such as pharmacy, metallurgy, and soapmaking. An appeal was also made for the setting up of what would virtually be a research organization, to effect rapid improvements in Science.

> The qualifications therefore required for our present purpose may be termed, Physical or Chemical Habits of judging about Things relating to Arts and Trades acquired by some competent Experience.... If choice were made of a Set of Men so qualified, and Rules given them to pursue, with due Care to register all their Experiments... so as to make an uniform and steady Business of the whole; there is good Reason to expect that in the compass of a few Years, considerable Improvements might be made in the present set of Arts and Sciences.

To some extent this appeal was answered by the foundation in 1754 of the Society for the Encouragement of Arts, Manufactures, and Commerce.

Shaw, the Physician

Shaw spent a considerable amount of his time for the next five years at Scarborough which had become extremely popular due in large part to the supposed efficacy of the Spa waters, and he was, in fact, instrumental in popularizing the resort. His practice at Scarborough was extremely successful, one of his patients being General Sutton (a friend of Lord Cuts and Bolingbroke, Sir Robert Walpole, and Dean Swift), who introduced him to Court circles.

Shaw was admitted Licentiate of the Royal College of Physicians on June 25, 1740, thereafter devoting himself almost entirely to medical pursuits. The last important work on chemistry to come from his pen was a new English translation (1741) of Boerhaave's "Elementa Chemiae" entitled, "A New Method of Chemistry." Shaw added numerous notes and references and "at the end of the second volume added his essays on the portable laboratory, on the scope of chemistry and on its application to the arts and manufacturers." This work was, without doubt, the most complete work on practical and theoretical chemistry in existence at the time and a third edition of it was printed in 1753.

Shaw rapidly rose to the top of the medical profession. In April, 1752, he was elected a Fellow of the Royal Society. In April, 1753, he was admitted a Candidate of the Royal College of Physicians and was made a Fellow one year later. He was, by now, Physician-Extraordinary to George II. The records show that he was now moving in very elegant circles indeed, but we are not really concerned here with his success in the field of medicine. Shaw's Chemical Lectures were the inspiration of such men as Peter Woulfe, Robert Dossie, D. W. Linden, and W. Lewis.

With the setting up of the Society for the Encouragement of Arts, Manufactures, and Commerce, Shaw was consulted with regard to problems suitable for pre-

miums. Among such subjects were the manufacture of ammonium chloride, high quality varnish, retorts and crucibles, and the purification of whale oil. Although Shaw was now too preoccupied with his medical duties to take a very active part in the society, he was undoubtedly consulted a great deal. The society, for example, was greatly interested in prospecting for cobalt in England, and Shaw's advice was frequently sought in this matter.

Although several of the members such as Lewis and Woulfe had their own laboratories, in 1756 it was felt that the society should have its own laboratory for the testing of materials, and again Shaw was called into consultation. Laboratories were, in fact, installed in the society building early in 1757.

Shaw's chemical lectures were reprinted in 1755 and translated into French and printed in Paris in 1759. There was, about this time, a revival of the practical study of chemistry, particularly in the universities of Glasgow, Edinburgh, and Cambridge. Richard Watson, appointed professor of chemistry at Cambridge in 1764 chose, as a theme for the university course, the application of chemistry to the arts and manufactures.

On December 11, 1760, Shaw was appointed Physician in Ordinary to George III, finally retiring on January 22, 1763. He died on March 15 of that year and was buried in the nave of Wimbledon church.

Conclusion

It is clear that by the middle of the eighteenth century England was in fact, on the verge of a second industrial revolution, the effects of which were, indeed, to be far-reaching. In the scientific world, the Royal Society, covering all branches of science, was supreme. This supremacy was now to be challenged by various technical societies, such as the Royal Society of Arts which had as one of its chief aims, as we have already seen, the encouragement of manufactures, commerce, and industrial arts. A new spirit was abroad and there was a vigorous development of the commercial applications of science, particularly in the field of industrial chemistry. In this field we owe a very great deal to the work of Peter Shaw.

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The Periodical Literature of Inorganic Chemistry

Since the end of World War II there has been a great increase of interest in inorganic chemistry. In 1948 only 9.9% of the papers abstracted by *Chemical Abstracts* (*CA*) were classified as inorganic. By 1958 this figure had reached 15.9%.[1] Larsen (*1*) has pointed out that the classification of papers as inorganic is a very subjective process. Part, but surely only a part, of this increase may be the result of a broader interpretation of the term "inorganic."

This increased productivity forces an increase in the attention paid to the inorganic literature by those who use it or are interested in chemical literature in general. In this paper an analysis of the periodical literature of the field is offered as an item of interest and aid to librarians, literature chemists, and inorganic chemists.

Leading Journals

The sources of the papers listed in the inorganic sections[2] of *Current Chemical Papers* (*CCP*) and *CA* for 1958 were tabulated. The count for *CA* included those papers in other sections for which a "see also" reference was given in section 6. The results are shown in Tables 1 and 2. Both lists were cut off at the 1% level.

A noteworthy feature is the very high rank of *Dissertation Abstracts* in both lists. Marr (*2*) estimates that only one half of thesis material is ever published. This means that approximately 1.5% of the abstracted inorganic literature is in the form of unpublished dissertations or the fragments left over after publication of the main results. Since only work from United States universities is covered in *Dissertation Abstracts* the over-all standing of dissertations in the inorganic literature must be quite a bit higher than shown here.

A large body of unavailable information seems to be indicated by the high rank of *Referativnyi Zhurnal, Khimiya* in the *CA* list.[3] Twenty-one, or 6.06%, of the 346 Russian papers abstracted came to *CA* indirectly via *Referativnyi Zhurnal*. Since the original papers were not available to *CA*, they are not likely to be readily acquired by anyone else in this country.

It is obvious that there is considerable agreement between *CA* and *CCP* as to the most important journals for inorganic chemistry in terms of volume. The correlation between the number of papers from a given journal which appeared in the inorganic sections of *CA* and *CCP* was calculated for the 41 leading journals, i.e., those which supplied at least 5 papers to either. The correlation coefficient was 0.92. A similar calculation for the 47 leading journals in *CCP* for 1957 and 1958 gave 0.91. The agreement between *CA* and *CCP* is, therefore, quite good. It could be improved

[1] From figures given in the Official Reports of the American Chemical Society for 1948 and 1958. *Chem. Eng. News*, Feb. 21, 1949, and March 9, 1959.

[2] Section 9 in *CCP* and section 6 in *CA*. Dr. Bernays of the Chemical Abstracts Services suggests that had section 18, Inorganic Industrial Chemicals, of *CA* been included, the *Zhur. Priklad. Khim.* would have appeared in Table 1.

[3] This abstract journal is not covered by *CCP*.

Table 1. Leading Inorganic Journals from Section 6 of CA for 1958

Rank	Journal[a]	No. of papers	Total, %
1	*Zhur. Neorg. Khim.*	160	9.15
2	*J. Am. Chem. Soc.*	143	8.17
3	*Z. anorg. u. allgem. Chem.*	105	6.01
4	*J. Chem. Soc.*	88	5.05
5	*Inorg. Syntheses*	66	3.78
6	*Compt. rend.*	51	2.92
7	*Dissertation Abstr.*	46	2.63
8	*J. Inorg. & Nuclear Chem.*	43	2.46
9	*Angew. Chem.*	37	2.12
10	*J. Indian Chem. Soc.*	31	1.77
11	*J. Phys. Chem.*	29	1.66
12	*Naturwissenschaften*	25	1.43
12	*J. Gen. Chem. U.S.S.R.*[b]	25	1.43
13	*Acta Chem. Scand.*	23	1.31
14	*Gazz. chim. ital.*	22	1.26
14	*Nippon Kagaku Zasshi (J. Chem. Soc. Japan)*	22	1.26
15	*Referat. Zhur, Khim.*	21	1.20
16	*Magyar Kém. Folyóirat*	19	1.09
16	*U.S. At. Energy Comm.*	19	1.09
17	*Bull. soc. chim. France*	18	1.03
18	*Chem. Ber.*	17	0.97
18	*Bull. Chem. Soc. Japan*	17	0.97
	245 other journals	720	41.24
	TOTAL	1747	

[a] The abbreviations authorized by *Chemical Abstracts* are used in this and other tables.

[b] This refers only to the English translation of the *Zhur. Obshchei Khim.* In order to avoid counting the same article twice the abstracts from the *Zhurnal* were not counted.

by making allowance for the fact that geochemical papers are treated as inorganic by *CCP* but not by *CA*.

Because of this agreement it is possible to produce a composite list of leading inorganic journals such as is shown in Table 3. The journals here are ordered on the basis of the sum of the papers supplied to *CA* and *CCP*. *Dissertation Abstracts* and *Inorganic Syntheses* are not included because they are not journals in the usual sense. These 17 journals include the top ten from each list. *Nature* and *Chemistry and Industry*, which do not appear on the *CA* list, are the only two which do not appear on both lists. Journal rankings in various other studies are also shown (*3–5*). The only two journals which did not appear on Brown's list of most cited journals (*5*) were not published at the time of that survey, 1954. Any library which already attempts to cover chemistry in general should have a good coverage of inorganic chemistry with the addition of the three specialized inorganic journals discussed below.

Language

The languages in which papers were written were tabulated for papers abstracted in section 6 (including cross references) of *CA*. The results are shown in Table 4. The relative rankings in organic and analytical chemistry, from Boig and Howerton (*3, 4*), are given along with the rank for chemistry as a whole. This over-all rank, reported by Heumann and Bernays (*6*), applies to the same volume of *CA* from which the data for the present study was taken (vol. **52,** 1958). Comparisons are more likely to be valid in this case than comparisons with the older Boig and Howerton rankings (1949–50). For this reason the percentage of abstracts from a given language for *CA* as a whole is also given in Table 4.

The general agreement between these various rankings is quite good. The most striking differences are: (1) the importance of Hungarian in the inorganic list; (2) the importance of Spanish and the absence of Polish in the analytical list; and (3) the absence of Czech from the organic list.

A strong inorganic specialization in German-speaking countries is shown by the fact that although only 9.7% of the abstracts in *CA* were of papers written in German, such papers supplied 16.62% of the abstracts in section 6. A similar, though less pronounced, specialization is apparent for Russian. In the case of Hungarian the number of papers involved is too small to make a valid judgment.

Of all the papers written in English, 11.4% appeared in journals for which English is not the normal language of publication, i.e., in journals such as the *Zeitschrift für physikalische Chemie*. Only 0.6% of the Russian papers appeared in journals outside the U.S.S.R. Of course within the Soviet there are many journals from areas where Russian is not the native language.

Specialized Journals

There are three journals which are primarily devoted to inorganic chemistry—the *Zeitschrift für anorganische und allgemeine Chemie* (founded 1892), the *Journal of Inorganic and Nuclear Chemistry* (1955), and the *Zhurnal Neorganicheskoi Khimii* (1956). These three journals account for about 20% of the inorganic papers in *CA* and *CCP*. Each has a distinct and characteristic "personality" which results not so much from typography and language as from the kind of research reported.

In order to study their differences issues 1, 4, 8, 10, and 12 of the 1958 *CCP* were scanned and the distribution of papers through the various sections of *CCP*

Table 2. Leading Inorganic Journals from Section 9 of CCP for 1958

Rank	Journal	No. of papers	Total, %
1	*J. Am. Chem. Soc.*	117	10.40
2	*Zhur. Neorg. Khim.*	106	9.45
3	*Z. anorg. u. allgem. Chem.*	80	7.11
4	*J. Chem. Soc.*	71	6.31
5	*J. Inorg. & Nuclear Chem.*	46	4.09
6	*Compt. rend.*	42	3.74
7	*Dissertation Abstr.*	38	3.38
7	*Angew. Chem.*	38	3.38
8	*J. Indian Chem. Soc.*	28	2.49
8	*Nature*	28	2.49
9	*J. Chem. Soc. Japan*	25	2.22
10	*Chem. & Ind. (London)*	23	2.04
11	*Chem. Listy*	21	1.86
12	*Doklady Akad. Nauk S.S.S.R.*	20	1.78
13	*Geokhimiya*	19	1.69
14	*Naturwissenschaften*	17	1.51
14	*Z. Naturforsch.*	17	1.51
14	*J. Phys. Chem.*	17	1.51
15	*Bull. soc. chim. France*	16	1.42
15	*Chem. Ber.*	16	1.42
16	*Zhur. Priklad. Khim.*	15	1.33
17	*Gazz. chim. ital.*	14	1.24
18	*Zhur. Obshchei Khim.*	13	1.15
19	*Geochim. et Cosmochim. Acta*	12	1.07
19	*Acta Chim. Acad. Sci. Hung.*	12	1.07
20	*Roczniki Chem.*	11	0.98
20	*Ricerca sci.*	11	0.98
	89 other journals	252	22.45
	TOTAL	1124	

Table 3. Composite List of Leading Inorganic Journals

Rank	Journal	Total papers in *CA* and *CCP*	Rank in other studies[a] Org.	Anal.	Total abstr.	Total cit.
1	*Zhur. Neorg. Khim.*	266	..	..	..	..
2	*J. Am. Chem. Soc.*	260	1	16	1	1
3	*Z. anorg. u. allgem. Chem.*	185	..	..	88	24
4	*J. Chem. Soc.*	159	2	..	4	2
5	*Compt. rend.*	93	8	15	3	8
6	*J. Inorg. & Nuclear Chem.*	89	..	..	..	..
7	*Angew. Chem.*	75	..	15	76	25
8	*J. Indian Chem. Soc.*	59	18	..	55	47
9	*J. Chem. Soc. Japan*	47	23	17	[b]	55
10	*J. Phys. Chem.*	46	..	..	30	23
11	*Naturwissenschaften*	42	..	..	21	48
12	*Nature*	41	9	10	7	11
13	*Zhur. Obschei Khim.*	38	3	..	16	29
14	*Gazz. chim. ital.*	36	11	..	..	34
15	*Bull. soc. chim. France*	34	6	6	26	7
16	*Chem. Ber.*	33	7	..	61	3
	Chem. & Ind. (London)	33	..	..	23	25

[a] Rank in organic and analytical chemistry (as of 1949 and 1950, respectively) is taken from BOIG AND HOWERTON (*3*, *4*).
[b] Pure chemistry Section, 20; Industrial Section, 9.
Rank in order of total number of abstracts appearing in *CA* during 1954 and rank in order of total number of times the journal was cited in a select sample of general chemical journals were taken from C. H. BROWN (*5*), pp. 51 and 98.

was noted.[4] Volume 8 of the *Journal* contained the Proceedings of the 1957 International Symposium of the Chemistry of Coordination Compounds and was not included in the count because it was not typical. As can be seen from Table 5, the distribution patterns are quite different.

The preponderance of papers from the *Zeitschrift* appear in section 9. This reflects the German emphasis on classical inorganic chemistry and supports the statement made by Audrieth and Otto (*7*) that "inorganic research in Germany is strongly concentrated on synthetic problems." The only other field that stands out in the *Zeitschrift* is that of phase studies.

The strong Russian emphasis on phase studies is very striking and shows the importance attached to physico-chemical analysis in the Soviet Union. There is also much more electrochemistry to be met with in the *Zhurnal* than in the others.

In the Anglo-American *Journal*[5] classical inorganic chemistry is again the leading category, but not by so wide a margin as in the *Zeitschrift*. The importance of studies on molecular properties (absorption spectra, magnetic properties, etc.) and reaction kinetics is much greater than in the other journals.

The *Journal* has the narrowest range of papers; it is represented in only seven sections of *CCP*, of which one is for nuclear chemistry, whereas the *Zeitschrift* and *Zhurnal* are represented in nine and ten sections, respectively. This may very well be due to the greater number and diversity of journals in Great Britain and the United States.[6]

[4] *Current Chemical Papers* is better suited for this than *Chemical Abstracts* because of the greater subdivision of physical chemistry in the former.

Table 4. Leading Languages in Which Inorganic Papers Are Written

Rank	Language	No. of abstracts	Total, %	Rank in Anal.	Org.	All Chem.	Percent of all Chem.
1	English	751	44.29	1	1	1	50.49
2	Russian	346	20.40	2	3	2	16.80
3	German	282	16.62	4	2	3	9.72
4	French	103	6.07	3	4	5	5.49
5	Japanese	55	3.24	6	6	4	6.10
6	Italian	52	3.07	8	5	6	3.58
7	Polish	30	1.77	..	8	8	1.52
8	Hungarian	18	1.06	14	12	11	<0.82
8	Czech	18	1.06	7	..	7	1.62
9	Spanish	16	0.94	5	7	9	1.02
	SUBTOTAL	1671	98.52[a]				

[a] Other languages represented are Chinese, Danish, Finnish, Norwegian, Romanian, Swedish, and Yugoslavian.

Table 5. Distribution of Papers from *Z. anorg. u. allgem. Chem.*, *J. Inorg. and Nuclear Chem.*, and *Zhur. Neorg. Khim.* among the Sections of *CCP*

Section no.	Name	No. of papers (and % of total) *Z.*		*J.*		*Zh.*	
1	Subatomics	0	(0.0)	10	(13.5)	1	(0.9)
2	Atomic and molecular properties	5	(6.0)	13	(17.6)	2	(1.7)
3	Phase structures and phase relations	14	(16.7)	0	(0.0)	54	(45.6)
4	Surface properties	3	(3.6)	0	(0.0)	0	(0.0)
6	Electrochemistry	3	(3.6)	4	(5.4)	16	(13.6)
7	Reaction kinetics and reaction mechanisms	1	(1.2)	11	(14.9)	4	(3.4)
8	Thermodynamics	5	(6.0)	0	(0.0)	2	(1.7)
9	Inorganic	51	(60.7)	30	(40.6)	35	(29.7)
10	Organic-organometallic and organometalloid	3	(3.6)	3	(4.1)	1	(0.9)
12	Analysis-inorganic	0	(0.0)	3	(4.1)	2	(1.7)
13	Apparatus and techniques	1	(1.2)	0	(0.0)	1	(0.9)
	TOTAL	86	(99.6)	74	(100.2)	118	(100.1)

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(4) *Ibid.*, **115**, 555 (1952).
(5) BROWN, C. H., "Scientific Serials," Association of College and Reference Libraries, Chicago, 1956.
(6) HEUMANN, K. F., AND BERNAYS, P. M., J. CHEM. EDUC., **36**, 478 (1959).
(7) AUDRIETH, L. F., AND OTTO, R. J., J. CHEM. EDUC., **36**, 441 (1959).

[5] Although an international journal, the great majority of its papers come from Great Britain or the United States.
[6] E. J. Crane, *Chem. Eng. News*, May 27, 1957, p. 94, reports that 2715 journals from Great Britain and the U.S.A. were abstracted by *CA* in 1956. The figures for Germany and the U.S.S.R. are 473 and 436, respectively.

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The Numerical Solution of Equations in Chemistry

Very frequently in the solving of chemical problems, an equation or a system of simultaneous equations cannot be solved explicitly for the desired unknown quantity. Occasionally it is possible to make some simplifying approximations in the equation or equations which then permit an approximate explicit solution. However, such approximations may introduce more error than is tolerable, and some other technique must then be used. It is the purpose of this paper to summarize some of the important equation-solving techniques of numerical analysis and to illustrate their application to chemical problems.

The Graphical Method

If it is desired to solve an equation of the form

$$f(x) = 0 \tag{1}$$

for the unknown quantity x, and it is found that it is impossible or too tedious to rearrange (1) into the form of $x =$ constant, then a plot can be made of $f(x)$ versus x, and the value of x where $f(x)$ is zero can be read directly from the plot.

Suppose for example that 0.5 mole of CO_2 gas at 200°C is confined in a 0.05-liter vessel, and it is desired to calculate the pressure of the gas under these conditions using the Kamerlingh Onnes equation of state for CO_2. If P is the pressure of the gas and V_m is the molar volume of the gas, this equation expresses the product PV_m in terms of a power series in P which is terminated after the fourth degree term, that is

$$PV_m = A + BP + CP^2 + DP^3 + EP^4 \tag{2}$$

By definition

$$V_m = \frac{V}{n} \tag{3}$$

where V is the total volume occupied by the gas and n is the number of moles of gas present. Thus

$$V_m = \frac{0.05 \text{ liter}}{0.5 \text{ mole}} = 0.1 \frac{\text{liter}}{\text{mole}}$$

For CO_2 at 200°C the coefficients in equation (2) have been found experimentally (*1*) for $0 \leq P \leq 1000$ atm. They are

$$A = 38.824 \frac{\text{atm liter}}{\text{mole}}$$

$$B = 1.3163 \times 10^{-2} \frac{\text{liter}}{\text{mole}}$$

$$C = 3.052 \times 10^{-5} \frac{\text{liter}}{\text{atm mole}}$$

$$D = -2.449 \times 10^{-8} \frac{\text{liter}}{\text{atm}^2 \text{ mole}}$$

$$E = 7.266 \times 10^{-12} \frac{\text{liter}}{\text{atm}^3 \text{ mole}}$$

Thus all the quantities in (2) are known except P. Equation (2) is easily rearranged into the form of (1) yielding

$$P^4 + \frac{D}{E} P^3 + \frac{C}{E} P^2 + \frac{B - V_m}{E} P + \frac{A}{E} = 0 \tag{4}$$

Substituting in the values of V_m, A, B, C, D, and E equation (4) becomes

$$(P) = P^4 - (3.3705 \times 10^3 \text{ atm})P^3 + (4.2004 \times 10^6 \text{ atm}^2)P^2 - (1.1951 \times 10^{10} \text{ atm}^3)P + (5.3432 \times 10^{12} \text{ atm}^4) = 0 \tag{5}$$

This is a quartic equation in P where the pressure is expressed in atmospheres.

An approximate value of P can be obtained by selecting values of P over a wide range, calculating $f(P)$ for each of these P values, constructing a plot of $f(P)$ versus P and estimating the value of P at which the curve crosses the P-axis. It is useful first, however, to obtain a rought estimate of P from the ideal gas law,

$$PV_m = RT \tag{6}$$

Solving for P yields

$$P = \frac{(0.08205 \text{ liter atm/deg mole})(473 \text{ deg})}{0.1000 \text{ liter/mole}} = 388 \text{ atm}$$

A more accurate value of P can now be found by calculating $f(P)$ for various values of P near 388 atm. The results of such calculations are shown in Table 1.

Table 1

P (atm)	$f(P)$ (atm^4)
300	$+2.053 \times 10^{12}$
400	$+1.045 \times 10^{12}$
500	$+0.059 \times 10^{12}$
600	-0.914×10^{12}

The values of P and $f(P)$ in Table 1 are plotted in Figure 1, and this graph shows that the value of P which makes $f(P)$ equal to zero is about 506 or 507 atm. A more accurate value of P could be found by making a similar plot of $f(P)$ versus P from $P = 505$ atm to $P = 508$ atm. On such an expanded scale the intersection of the curve with the P axis could be estimated much more accurately.

Although the graphical method may in this way be extended to give the desired accuracy, computing time and labor can usually be saved if graphical methods are used only to find approximate solutions and other numerical techniques are then introduced to find a more refined or accurate solution.

The Method of False Position

The next numerical method of solving equations that is to be considered here is the method of false position.

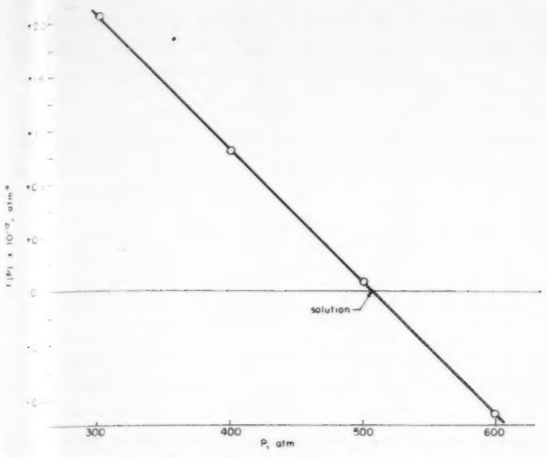

Figure 1. An approximate graphical solution of equation (5).

This is also referred to as the method of linear interpolation. The technique consists of finding two values of x in the neighborhood of the solution of the equation $(x) = 0$. These values are chosen on opposite sides of the root of the equation and are used to determine a linear approximation to the function in the neighborhood of the root. The solution is then found to the linear approximation and is used as an approximate root of $f(x) = 0$. The procedure involved is pictured in Figure 2, which shows a plot of $f(x)$ versus x. The root, r, of $f(x) = 0$ is the intersection of the curve with the x-axis. x_0 and a are values of x on either side of r. To obtain an approximate value of r, a linear interpolation is made from the point A to the point B. Clearly the slope of the line $\overline{AB}$ is given either by $[0 - f(x_0)]/(x_1 - x_0)$ or $[f(a) - 0]/(a - x_1)$. Thus

$$\frac{-f(x_0)}{x_1 - x_0} = \frac{f(a)}{a - x_1}$$

If this equation is solved for x_1,

$$x_1 = \frac{af(x_0) - x_0 f(a)}{f(x_0) - f(a)} \tag{7}$$

This gives x_1 in terms of x_0 and a. Although equation (7) is entirely suitable for calculating x_1, it can be rearranged into a form which is simpler for calculating purposes. This is done by first adding and subtracting $x_0 f(x_0)$ in the numerator of (7), which yields

$$x_1 = \frac{af(x_0) - x_0 f(x_0) + x_0 f(x_0) - x_0 f(a)}{f(x_0) - f(a)}$$

$$= \frac{(a - x_0)f(x_0) + x_0[f(x_0) - f(a)]}{f(x_0) - f(a)}$$

Dividing numerator and denominator by $f(x_0) - f(a)$ gives the result

$$x_1 = x_0 + \frac{(a - x_0)f(x_0)}{f(x_0) - f(a)} \tag{8}$$

Equation (8) has the advantage over (7) that it expresses x_1 as x_0 + a correction, and thus if the correction is of a much smaller order of magnitude than x_0 it usually need not be carried out to as many significant figures as x_0 contains. If x_1 is still not a satisfactory approximation of r then an even better approximation, x_2, can be found from

$$x_2 = x_1 + \frac{(a - x_1)f(x_1)}{f(x_1) - f(a)} \tag{9}$$

This calculation can be repeated for further improvement as many times as necessary and in general the nth approximation to r can be used to obtain the $(n + 1)$th approximation from the equation

$$x_{n+1} = x_n + \frac{(a - x_n)f(x_n)}{f(x_n) - f(a)} \tag{10}$$

The sequence of numbers generated from (10) will then converge on the value of r.

The use of equation (8) will now be illustrated by finding a more accurate solution to equation (5) than was found earlier by the graphical method. First, two values of P (x_0 and a) must be found such that one gives a positive value and the other gives a negative value of $f(P)$. Recall that the graphical solution to (5) indicated that P is about 506 or 507 atm. It is discovered by trial that

$$f(506 \text{ atm}) = +3.5 \times 10^8 \text{ atm}^4$$

and

$$f(507 \text{ atm}) = -9.43 \times 10^8 \text{ atm}^4$$

Thus 506 and 507 atm are suitable for linear interpolation of equation (5). Using (8) an improved value of P is found to be

$$P = 506 \text{ atm} + \frac{(507 \text{ atm} - 506 \text{ atm})(3.5 \times 10^8 \text{ atm}^4)}{(3.5 \times 10^8 \text{ atm}^4) - (-9.43 \times 10^8 \text{ atm}^4)}$$

$$= 506 \text{ atm} + 0.036 \text{ atm}$$

$$= 506.036 \text{ atm}$$

Recording significant figures beyond the decimal place is justified here since 506 atm is an exact number. To check this root and to see whether another linear interpolation is advisible, $P = 506.036$ atm is substituted into equation (2) which gives

$$(506.036)(0.1) \stackrel{?}{=} 38.824 + (1.3163 \times 10^{-2})(506.036) + (3.052 \times 10^{-5})(506.036)^2 + (-2.449 \times 10^{-8})(506.036)^3 + (7.266 \times 10^{-12})(506.036)^4$$

or

$$50.6036 \doteq 50.6033$$

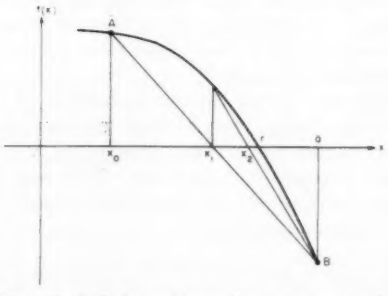

Figure 2. The method of false position and its convergence on the root of an equation.

The check is satisfactory and the root obtained can be rounded off to the proper number of significant figures. The original data indicate that this is four or possibly five figures. Thus the solution is

$$P = 506.04 \text{ atm}$$

The Method of Iteration

Another method for the numerical solution of equations is the method of iteration. This technique can be used to solve both single equations and systems of

simultaneous equations. To solve an equation of the type

$$f(x) = 0 \tag{11}$$

it is necessary first to rearrange (11) into the form

$$x = F(x) \tag{12}$$

Then if x_0 is an approximate value of the root of (11), perhaps obtained from a graph or even an educated guess, very often an even better approximation to the root, x_1, can be obtained from (12), as

$$x_1 = F(x_0) \tag{13}$$

A further improvement is then

$$x_2 = F(x_1) \tag{14}$$

and so on, the general relationship being

$$x_{n+1} = F(x_n) \tag{15}$$

This process of iteration is illustrated in Figure 3.

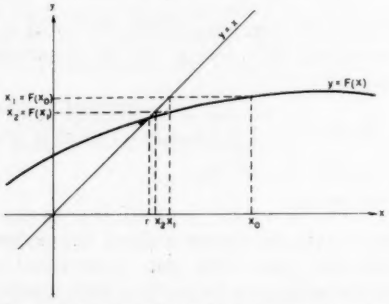

Figure 3. The method of iteration and its convergence on the root of an equation.

Solving the equation $x = F(x)$ is equivalent to solving the two simultaneous equations $y = x$ and $y = F(x)$, and the solution is the intersection of these two curves. As Figure 3 shows, x_0 can be used to calculate $x_1 = F(x_0)$, shown on the y azis. Then using the $y = x$ curve, x_1 can be placed on the x-axis and used to calculate $x_2 = F(x_1)$. The method of iteration will not always work, however, and a case where convergence will not occur is shown in Figure 4.

To illustrate the use of the technique of iteration, consider the problem of finding the temperature at which *o*-toluidine has a vapor pressure of 500 mm Hg. The vapor pressure of *o*-toluidine (*2*) in mm Hg, p, is known as an empirical function of the absolute temperature, T. The relationship is

$$\log p = 23.8296 - \frac{3480.3}{T} - 5.081 \log T \tag{16}$$

If $p = 500$ mm, then (16) becomes

$$\log (500) = 23.8296 - \frac{3480.3}{T} - 5.081 \log T \tag{17}$$

Equation (17) can then be written as

$$f(T) = 21.1306 - \frac{3480.3}{T} - 5.081 \log T = 0 \tag{18}$$

To find the approximate value of T which satisfies (18), $f(T)$ is calculated for values of T from 300 to 600 degrees on the absolute scale. The results of these calculations are shown in Table 2 and are plotted in Figure 5.

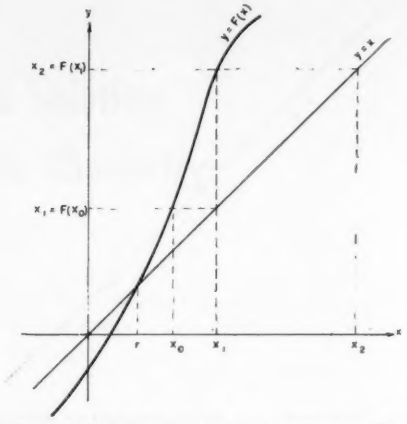

Figure 4. A case where iteration does not converge on the root of an equation.

Table 2

T, (°K)	$f(T)$
300	−3.0566
350	−1.7395
400	−0.7912
450	−0.0844
500	+0.4565
550	+0.8790
600	+1.2143

The plot shows that the solution to (18) is about T = 460 deg. In order to apply the method of iteration, (18) is rearranged into the form $T = F(T)$ as

$$T = \frac{3480.3}{21.1306 - 5.081 \log T} \tag{19}$$

Equation (19) is then used to calculate successively better values of T, beginning with $T = 460$ degrees. The calculations involved are shown in Table 3. Since

Table 3

T	5.081 log T	21.1306 − 5.081 log T	3480.3/(21.1306 − 5.081 log T)
460	13.5295	7.6011	457.87
457.87	13.5192	7.6114	457.25
457.25	13.5162	7.6144	457.07
457.07	13.5154	7.6152	457.02
457.02	13.5152	7.6154	457.01
457.01	13.5151	7.6153	457.01

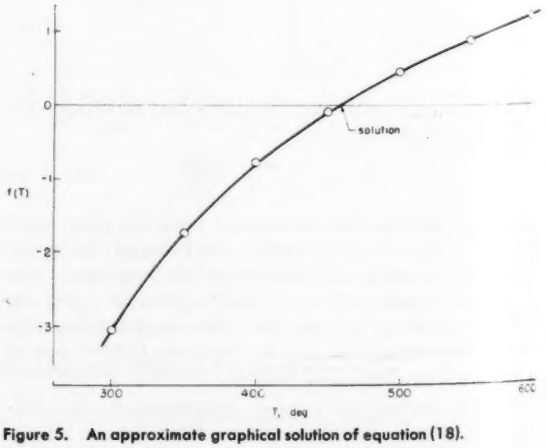

Figure 5. An approximate graphical solution of equation (18).

the original data justifies a solution to about five significant figures, and since the 6th and 7th approximations to T agree to two decimal places,

$$T = 457.01 \text{ deg}$$

A check on this value can easily be made by substituting $p = 500$ mm and $T = 457.01$ deg into equation (16). The result is

$$\log (500) \stackrel{?}{=} 23.8296 - \frac{3480.3}{457.01} - 5.081 \log (457.01)$$

or

$$2.6990 \doteq 2.6991$$

The method of iteration can easily be generalized to several equations in several unknowns. For example if it is desired to solve the two equations

$$\left.\begin{aligned} f(x,y) &= 0 \\ g(x,y) &= 0 \end{aligned}\right\} \tag{20}$$

simultaneously, they are first rearranged into the form

$$\left.\begin{aligned} x &= F(x,y) \\ y &= G(x,y) \end{aligned}\right\} \tag{21}$$

Then successively better approximations to the values of x and y which satisfy (20) can be found from the first approximations x_0 and y_0, as

$$\left.\begin{aligned} x_1 &= F(x_0,y_0) \\ y_1 &= G(x_1,y_0) \end{aligned}\right\}$$

Similarly the next improvement is

$$\left.\begin{aligned} x_2 &= F(x_1,y_1) \\ y_2 &= G(x_2,y_1) \end{aligned}\right\}$$

and so on until the desired accuracy is reached. Notice that x_n, instead of x_{n-1}, is used in finding y_n.

To solve three equations in three unknowns

$$\left.\begin{aligned} f(x,y,z) &= 0 \\ g(x,y,z) &= 0 \\ h(x,y,z) &= 0 \end{aligned}\right\} \tag{22}$$

the equations are similarly rearranged to

$$\left.\begin{aligned} x &= F(x,y,z) \\ y &= G(x,y,z) \\ z &= H(x,y,z) \end{aligned}\right\} \tag{23}$$

and improvements on the first approximations to the solution, x_0, y_0 and z_0, are obtained from the equations

$$\left.\begin{aligned} x_1 &= F(x_0,y_0,z_0) \\ y_1 &= G(x_1,y_0,z_0) \\ z_1 &= H(x_1,y_1,z_0) \end{aligned}\right\}$$

Similarly

$$\left.\begin{aligned} x_2 &= F(x_1,y_1,z_1) \\ y_2 &= G(x_2,y_1,z_1) \\ z_2 &= H(x_2,y_2,z_1) \end{aligned}\right\}$$

and so on. The technique is easily generalized to any number of equations involving the same number of unknowns.

As an illustration the mathematical description of the species present in a 0.5000 molal acetic acid-water solution at 25°C may be considered. The equilibrium constant expressions for the two equilibria which exist in the system are

$$K_a = \frac{\gamma_{H^+}\{H^+\}\gamma_{Ac^-}\{Ac^-\}}{\gamma_{HAc}\{HAc\}} \tag{24}$$

for the dissociation of acetic acid, and

$$K_w = \gamma_{H^+}\{H^+\}\gamma_{OH^-}\{OH^-\} \tag{25}$$

for the dissociation of water. In these two expressions $\{J\}$ represents the molal concentration of the species J in moles of J per kg of solvent and γ_J is the activity coefficient of J on a molal basis. The law of electrical neutrality for this solution is

$$\{H^+\} = \{Ac^-\} + \{OH^-\} \tag{26}$$

and the total molal concentration of acid, m_a, is given by

$$m_a = \{HAc\} + \{Ac^-\} \tag{27}$$

Since the solution is dilute, an expression for the activity coefficients can be obtained from the Debye-Hückel limiting law which states that

$$\log \gamma_J = -z_J^2 A\sqrt{\mu} \tag{28}$$

where z_J is the charge on the ionic species, J, A is a constant at a given temperature, and μ is the ionic strength of the solution, defined as

$$\mu = {}^1/_2 \sum_J z_J^2\{J\} \tag{29}$$

where the summation is carried out over all the different ionic species J. Applying (29) to the acetic acid solution under consideration yields

$$\mu = {}^1/_2 (\{H^+\} + \{Ac^-\} + \{OH^-\}) \tag{30}$$

and substitution of (26) into (30) yields the simpler expression

$$\mu = \{H^+\} \tag{31}$$

Since $z_J^2 = 1$ for H^+, Ac^- and OH^-, (28) yields the same values for γ_{H^+}, γ_{Ac^-}, and γ_{OH^-}. This common value will be represented by γ, and from (28) and (31)

$$\log \gamma = -A\sqrt{\{H^+\}} \tag{32}$$

Also since $\gamma_{H^+} = \gamma_{Ac^-} = \gamma_{OH^-} = \gamma$ and since γ_{HAc} is nearly unity, (24) and (25) can be written as

$$K_a = \frac{\gamma^2\{H^+\}\{Ac^-\}}{\{HAc\}} \tag{33}$$

and

$$K_w = \gamma^2\{H^+\}\{OH^-\} \tag{34}$$

Equations (26), (27), (32), (33), and (34) are five equations in the five unknowns $\{H^+\}$, $\{Ac^-\}$, $\{OH^-\}$, $\{HAc\}$, and γ, and they may be solved simultaneously by the method of iteration, using the data: $K_w = 1.008 \times 10^{-14}$ (*3*), $A = 0.5085$ kg$^{1/2}$ mole$^{-1/2}$(*4*), $m_a = 0.5000$ mole kg^{-1}, and $K_a = 1.754 \times 10^{-5}$ (*5*). To apply this method each of the equations listed above is solved for one of the unknowns appearing in the equation. Shown below are equations (33), (32), (34), (26), and (27), rearranged into one possible form in the order listed.

$$\{H^+\} = \frac{K_a\{HAc\}}{\gamma^2\{Ac^-\}} = \frac{1.754 \times 10^{-5}\{HAc\}}{\gamma^2\{Ac^-\}} \tag{35}$$

$$\gamma = 10^{-A\sqrt{\{H^+\}}} = 10^{-0.5085\sqrt{\{H^+\}}} \tag{36}$$

$$\{OH^-\} = \frac{K_w}{\gamma^2\{H^+\}} = \frac{1.008 \times 10^{-14}}{\gamma^2\{H^+\}} \tag{37}$$

$$\{Ac^-\} = \{H^+\} - \{OH^-\} \tag{38}$$

$$\{HAc\} = m_a - \{Ac^-\} = 0.5000 - \{Ac^-\} \tag{39}$$

Note that if a first approximation of $\{H^+\}$ were available, the first approximations of the other unknowns

could be calculated from (36)–(39). This approximate value of $\{H^+\}$ can be found by the following procedure. $\{Ac^-\}$ in (27) and $\{OH^-\}$ in (26) are neglected as being very small. This yields $m_a \simeq \{HAc\}$ and $\{H^+\} \simeq \{Ac^-\}$. Substituting these two equations into (33) and assuming that $\gamma \simeq 1$ yields $K_a \simeq \{H^+\}^2/m_a$. Solving for $\{H^+\}$ produces

$$\{H^+\} \simeq \sqrt{K_a m_a} = \sqrt{(1.754 \times 10^{-5})(0.5000)} \text{ mole kg}^{-1}$$
$$= 2.9614 \times 10^{-3} \text{ mole kg}^{-1}$$

This approximate value of $\{H^+\}$ gives a starting point for the process of iteration. The calculations which are necessary using (35)–(39) are shown in Table 4. By inspection of the first three values of $\{H^+\}$ in Table 4 it is seen that the successive approximations are alternating back and forth and that the convergence of this process is extremely slow. Unfortunately, this is sometimes a characteristic of the method of iteration. To speed up the convergence, the 2nd and 3rd approximations of $\{H^+\}$ were averaged, and this intermediate value of $\{H^+\}$ was used as the 4th approximation. After two further calculations and two averaging operations, successive solutions are found to agree to five significant figures. The final answers are

$$\begin{aligned} \{H^+\} &= 3.153 \times 10^{-3} \text{ mole kg}^{-1} \\ \gamma &= 0.9364 \\ \{OH^-\} &= 3.647 \times 10^{-9} \text{ mole kg}^{-1} \\ \{Ac^-\} &= 3.153 \times 10^{-3} \text{ mole kg}^{-1} \\ \{HAc\} &= 0.4968 \text{ mole kg}^{-1} \end{aligned}$$

where the values are rounded off to four significant figures. Equation (28) is usually considered to be accurate only for solutions where $\mu \leq 0.01$ mole kg^{-1}. Since $\{H\} = \mu = 0.003153$ mole kg^{-1}, the use of this equation is justified.

Finally these results should be substituted into equations (26), (27), (32), (33), and (34) to see if they check properly. This is important since there was no assurance that the successive approximations would actually converge to the solution in this case. Substituting the solution into the above equations in the order listed shows that

$$3.153 \times 10^{-3} \stackrel{?}{=} 3.153 \times 10^{-3} + 3.647 \times 10^{-9}$$
$$= 3.153 \times 10^{-3}$$

$$0.5000 \stackrel{?}{=} 0.4968 + 3.153 \times 10^{-3}$$
$$= 0.5000$$

$$\log(0.9364) = -0.5085\sqrt{3.153 \times 10^{-3}}$$
$$-0.02854 = -0.02855$$

$$1.754 \times 10^{-5} \stackrel{?}{=} \frac{(0.9364)^2(3.153 \times 10^{-3})(3.153 \times 10^{-3})}{0.4968}$$
$$= 1.755 \times 10^{-5}$$

$$1.008 \times 10^{-14} \stackrel{?}{=} (0.9364)^2(3.153 \times 10^{-3})(3.647 \times 10^{-9})$$
$$= 1.008 \times 10^{-14}$$

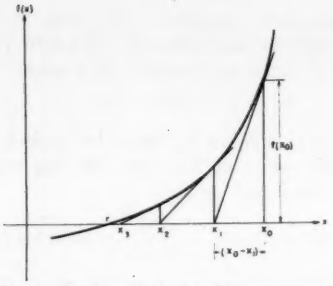

Figure 6. The Newton-Raphson Method and its convergence on the root of an equation.

The check verifies that the solution obtained satisfies the original system of equations.

The Newton-Raphson Method

This technique also involves successive improvement of an approximate solution. To solve a single equation of the type

$$f(x) = 0 \tag{40}$$

a first guess or approximation, x_0, is made for the root, r, of equation (40). Figure 6 shows a plot of $f(x)$ versus x. x_0 is then improved by considering the tangent to $f(x)$ at the point $(x_0, f(x_0))$. This tangent is extended until it intersects the x-axis at $x = x_1$, where x_1 is a better approximation to r than x_0. The tangent described has a slope denoted by $f'(x_0)$, that is, the first derivative of $f(x)$ evaluated at $x = x_0$. From Figure 6 it can be seen that this slope is $f(x_0)/(x_0 - x_1)$. Thus

$$f'(x_0) = \frac{f(x_0)}{x_0 - x_1} \tag{41}$$

Solving (41) for x_1 yields

$$x_1 = x_0 - \frac{f(x_0)}{f'(x_0)} \tag{42}$$

Similarly, x_2 can be obtained from x_1 by

$$x_2 = x_1 - \frac{f(x_1)}{f'(x_1)} \tag{43}$$

In general, the $(n + 1)$th approximation to r can be obtained from the nth approximation to r by the relationship

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)} \tag{44}$$

The Newton-Raphson method will not always generate a series of numbers which converge to the desired root. A case where no convergence occurs is shown in Figure 7.

Table 4

$\{H^+\} = \frac{1.754 \times 10^{-5}\{HAc\}}{\gamma^2\{Ac^-\}}$	$\gamma = 10^{-0.5085\sqrt{\{H^+\}}}$	$\{OH^-\} = \frac{1.008 \times 10^{-14}}{\gamma^2\{H^+\}}$	$\{Ac^-\} = \{H^+\} - \{OH^-\}$	$\{HAc\} = 0.5000 - \{Ac^-\}$
2.9614×10^{-3}	0.93828	3.8664×10^{-9}	2.9614×10^{-3}	0.49704
3.3440×10^{-3}	0.93452	3.4516×10^{-9}	3.3440×10^{-3}	0.49666
2.9829×10^{-3}				
3.1635×10^{-3a}	0.93626	3.6349×10^{-9}	3.1635×10^{-3}	0.49684
3.1425×10^{-3}				
3.1530×10^{-3a}	0.93637	3.6462×10^{-9}	3.1530×10^{-3}	0.49685
3.1524×10^{-3}				
3.1527×10^{-3a}	0.93637	3.6465×10^{-9}	3.1527×10^{-3}	0.49685
3.1526×10^{-3}	0.93637	3.6467×10^{-9}	3.1526×10^{-3}	0.49685

[a] This value obtained by averaging the last two values.

To illustrate the use of the Newton-Raphson method in solving one equation in one unknown, the following problem may be considered. Suppose a radioactive nuclide A decays into another radioactive nuclide B, and B in turn further decays. If the half lives of A and B, τ_A and τ_B, are 8.000 days and 2.000 days respectively, how long would it take for 10^{20} nuclides of pure A isotope to produce 10^{19} nuclides of B, if at time $t = 0$ the number of B nuclides is zero? If N_A and N_B are the number of A and B nuclides at any time t and N_A^0 and N_B^0 are the number of A and B nuclides at $t = 0$, then $N_A^0 = 10^{20}$ nuclides and $N_B^0 = 0$. If the appropriate

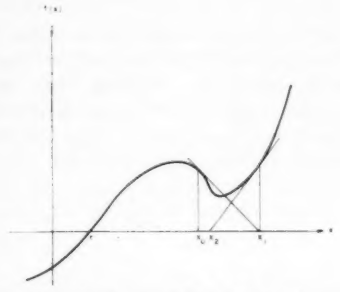

Figure 7. A case where the Newton-Raphson Method does not converge on the root of an equation.

rate equation for the decay scheme

$$A \xrightarrow{\tau_A = 8 \text{ days}} B \xrightarrow{\tau_B = 2 \text{ days}} C$$

is solved under the boundary conditions that, at $t = 0$, $N_A = N_A^0$ and $N_B = N_B^0 = 0$, then the equation for the variation of N_B with time is found to be

$$N_B = \left(\frac{\lambda_A N_A^0}{\lambda_B - \lambda_A}\right)(e^{-\lambda_A t} - e^{-\lambda_B t}) \tag{45}$$

where λ_A and λ_B are the rate constants for the decay of A and B, respectively. The rate constants are related to the half lives by

$$\lambda = \frac{\ln 2}{\tau} \tag{46}$$

Thus

$$\lambda_A = \frac{\ln 2}{T_A} = \frac{0.693147}{8.000 \text{ day}} = 0.0866434 \text{ day}^{-1}$$

and

$$\lambda_B = \frac{\ln 2}{T_B} = \frac{0.693147}{2.000 \text{ day}} = 0.346574 \text{ day}^{-1}$$

Thus all the quantities in (45) are known except for the time t which is required to make $N_B = 10^{19}$ nuclides. Rearranging (45) gives

$$e^{-\lambda_A t} - e^{-\lambda_B t} = \frac{N_B}{N_A^0}\,\frac{\lambda_B - \lambda_A}{\lambda_A} \tag{47}$$

Evaluation of the right-hand side of (47) yields

$$e^{-\lambda_A t} - e^{-\lambda_B t} = 0.3000 \tag{48}$$

To obtain an approximate value of the root of this equation, $e^{-\lambda_A t} - e^{-\lambda_B t}$ is plotted against t, as shown in Figure 8. This curve is proportional to a plot of N_B versus t and indicates that $e^{-\lambda_A t} - e^{-\lambda_B t}$ takes on the value 0.3000 at two different times, and these are seen from the plot to be approximately 1.6 days and 13.5 days. To improve these approximate roots, (48) is rearranged into the proper form for the application of the Newton-Raphson method, namely

$$f(t) = e^{-\lambda_A t} - e^{-\lambda_B t} - 0.3000 = 0 \tag{49}$$

The derivative of $f(t)$ is then

$$f'(t) = -\lambda_A e^{-\lambda_A t} + \lambda_B e^{-\lambda_B t} \tag{50}$$

These functions are then used as prescribed by equation (44) where the quotient $f(t)/f'(t)$ is a correction for the improvement of the first approximation. The calculations for improving the smaller root are shown in Table 5. As can be seen only three improvements on the first approximation of $t = 1.6$ days were required to obtain the smaller of the two roots to five decimal places, namely 1.63097 days. Rounding off to four significant figures gives a value of 1.631 days. If the same procedure is used on the larger root, the answer is found to be 13.550 days.

Table 5

t (day)	$f(t)$	$f'(t)$ (day^{-1})	$f(t)/f'(t)$ (day)
1.6	−0.003783	0.123628	−0.03060
1.63060	−0.000045	0.121726	−0.00037
1.63097	0.000000	0.121704	0.00000

Before presenting the Newton-Raphson method for the solution of simultaneous systems of equations, it will be profitable to consider a more rigorous derivation of this method for a single equation. The approximation is made that x_0 is near the root, r, of

$$f(x) = 0 \tag{51}$$

It is desired to find a correction, Δx, for x_0, such that $r = x_0 + \Delta x$, that is,

$$f(x_0 + \Delta x) = 0 \tag{52}$$

The left-hand side of (52) can be written as a Taylor series expansion of the function about the point x_0,

$$f(x_0) + f'(x_0)\Delta x + f''(x_0)\frac{(\Delta x)^2}{2!} + \ldots = 0 \tag{53}$$

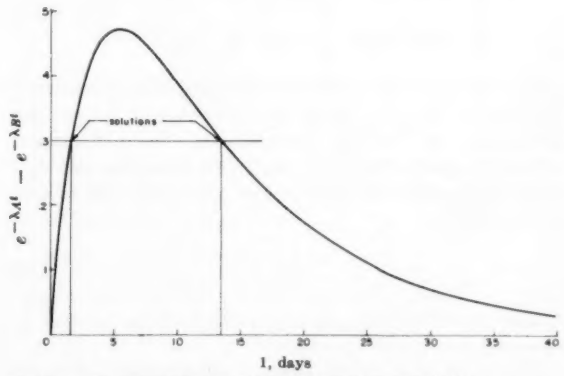

Figure 8. An approximate graphical solution of equation (48).

If the initial approximation, x_0, is fairly close to r, then Δx is small and terms involving Δx raised to a power can be neglected. This leaves the approximate equation for Δx

$$f(x_0) + f'(x_0)\Delta x \simeq 0 \tag{54}$$

or if (54) is rearranged and written as an exact equation

$$f'(x_0)\Delta x_0 = -f(x_0) \tag{55}$$

where the correction is written as Δx_0 rather than Δx since Δx does not exactly satisfy (55). Then (55) can be solved for Δx_0 and this correction can be used to calculate the better approximation

$$x_1 = x_0 + \Delta x_0 \tag{56}$$

Then x_1 can be improved in the same way that x_0 was, that is, by finding a correction Δx_1 from

$$f'(x_1)\Delta x_1 = -f(x_1) \tag{57}$$

and calculating

$$x_2 = x_1 + \Delta x_1$$

The process is continued until the desired degree of accuracy is obtained.

The technique for solving two equations in two unknowns can be developed in an entirely analogous fashion. Suppose that x_0 and y_0 is a first approximation to the solution of two simultaneous equations

$$\left.\begin{aligned} f(x,y) &= 0 \\ g(x,y) &= 0 \end{aligned}\right\} \tag{58}$$

Again a correction Δx and Δy is sought such that

$$\left.\begin{aligned} f(x_0 + \Delta x,\ y_0 + \Delta y) &= 0 \\ g(x_0 + \Delta y,\ y_0 + \Delta y) &= 0 \end{aligned}\right\} \tag{59}$$

These two equations may be written as a Taylor series expansion for functions of two variables about the point (x_0, y_0),

$$\left.\begin{aligned} f(x_0,y_0) + \frac{\partial}{\partial x} f(x_0,y_0)\Delta x + \frac{\partial}{\partial y} f(x_0, y_0)\Delta y + \ldots &= 0 \\ g(x_0,y_0) + \frac{\partial}{\partial x} g(x_0, y_0)\ \Delta x + \frac{\partial}{\partial y} g(x_0,y_0)\ \Delta y + \ldots &= 0 \end{aligned}\right\} \tag{60}$$

If terms of higher order than the first are neglected then equations (60) can be rearranged into

$$\left.\begin{aligned} \frac{\partial}{\partial x} f(x_0,y_0)\Delta x_0 + \frac{\partial}{\partial y} f(x_0,y_0)\Delta y_0 &= -f(x_0),y_0) \\ \frac{\partial}{\partial x} g(x_0,y_0)\Delta x_0 + \frac{\partial}{\partial y} g(x_0,y_0)\Delta y_0 &= -g(x_0,y_c) \end{aligned}\right\} \tag{61}$$

where the corrections are written as Δx_0 and Δy_0 since they do not exactly satisfy the definition of Δx and Δy. Equations (61) are two simultaneous linear equations which are easily solved for the corrections Δx_0 and Δy_0. Improved approximations to the roots can then be calculated from

$$\left.\begin{aligned} x_1 &= x_0 + \Delta xo \\ y_1 &= y_0 + \Delta yo \end{aligned}\right\} \tag{62}$$

x_1 and y_1 can be simlarly improved and the process repeated as often as necessary.

The method is easily generalized further. For example, if x_0, y_0, and z_0 are first approximations to the solution of the three simultaneous equations

$$\left.\begin{aligned} f(x,y,z) &= 0 \\ g(x,y,z) &= 0 \\ h(x,y,z) &= 0 \end{aligned}\right\} \tag{63}$$

then the corrections for improving these are found by solving the three linear simultaneous equations

$$\left.\begin{aligned} \frac{\partial}{\partial x} f(x_0,y_0,z_0)\ \Delta x_0 + \frac{\partial}{\partial y} f(x_0,y_0,z_0)\ \Delta y_0 + \frac{\partial}{\partial z} f(x_0,y_0,z_0)\ \Delta z_0 &= -f(x_0,y_0,z_0) \\ \frac{\partial}{\partial x} g(x_0,y_0,z_0)\ \Delta x_0 + \frac{\partial}{\partial y} g(x_0,y_0,z_0)\ \Delta y_0 + \frac{\partial}{\partial z} g(x_0,y_0,z_0)\ \Delta z_0 &= -g(x_0,y_0,z_0) \\ \frac{\partial}{\partial x} h(x_0,y_0,z_0)\ \Delta x_0 + \frac{\partial}{\partial y} h(x_0,y_c,z_0)\ \Delta y_0 + \frac{\partial}{\partial z} h(x_0,y_c,z_0)\ \Delta z_0 &= -h(x_0,y_0,z_0) \end{aligned}\right\} \tag{64}$$

for Δx_0, Δy_0, and Δz_0. The improved approximate solution is then

$$\left.\begin{aligned} x_1 &= x_0 + \Delta x_c \\ y_1 &= y_0 + \Delta y_0 \\ z_1 &= z_0 + \Delta z_0 \end{aligned}\right\} \tag{65}$$

The use of the Newton-Raphson method to solve a system of simultaneous equations will be illustrated by an equilibrium problem. Suppose that an aqueous solution contains 5.000×10^{-3} moles of sodium acetate, NaAc, per kg of water and is at a temperature of 25°C. The equilibrium constant expressions are

$$K_a = \frac{\gamma^2\{H^+\}\{Ac^-\}}{\{HAc\}} \tag{66}$$

and

$$K_w = \gamma^2\{H^+\}\{OH^-\} \tag{67}$$

where γ is the activity coefficient of any of the ions in the system. The electrical neutrality equation is

$$\{Na^+\} + \{H^+\} = \{Ac^-\} + \{OH^-\} \tag{68}$$

The number of moles of sodium acetate per kg of water, m_s, is given by

$$m_s = \{Na^+\} \tag{69}$$

and

$$m_s = \{HAc\} + \{Ac^-\} \tag{70}$$

The ionic strength of the solution is

$$\mu = {}^1/_2(\{Na^+\} + \{H^+\} + \{Ac^-\} + \{OH^-\}) \tag{71}$$

This can be simplified by the substitution of (68) and (69) into (71), which yields

$$\mu = m_s + \{H^+\} \tag{72}$$

Thus, γ, as given by the Debye-Hückel limiting law, is

$$\log \gamma = -A\sqrt{m_s + \{H^+\}} \tag{73}$$

Finally (69) can be substituted into (68), which yields

$$m_s + \{H^+\} = \{Ac^-\} + \{OH^-\} \tag{74}$$

Equations (66), (67), (70), (73), and (74) then represent five equations in the five unknowns γ, $\{H^+\}$, $\{OH^-\}$, $\{Ac^-\}$, and $\{HAc\}$, which can be solved simultaneously by the use of the Newton-Raphson method. A considerable simplification can first be made, however. In adding NaAc to water, in which the equilibrium $H_2O = H^+ + OH^-$ is assumed to exist, the acetate ions from the salt react with the hydrogen ions already in the water according to the equilibrium $HAc = H^+ + Ac^-$. Thus the addition of Ac^- will, according to Le Chatelier's principle, decrease the number of H^+ ions and increase the number of OH^- ions in the solution. Since $\{H^+\} \simeq 10^{-7}$ mole kg^{-1} in pure water, it then follows that $\{H^+\} < 10^{-7}$ mole kg^{-1} in this solution. Since $m_s = 5.000 \times 10^{-3}$ mole kg^{-1}, $\{H^+\}$ is

negligible compared to m_s in equation (73). Thus it is possible to calculate γ from the approximation

$$\log \gamma = -A\sqrt{m_s} \tag{75}$$

to a high degree of accuracy. Using A = 0.5085 $kg^{1/2}$ $mole^{-1/2}$ and $m_s = 5.000 \times 10^{-3}$ mole kg^{-1}, (75) yields

$$\gamma = 10^{-0.5085\sqrt{0.005000}} = 0.92054 \tag{76}$$

Now equations (66), (67), (70), and (74) make up a simpler system of four equations in four unknowns, $\{H^+\}$, $\{OH^-\}$, $\{Ac^-\}$, and $\{HAc\}$. In these equations γ is known and $K_a = 1.754 \times 10^{-5}$, $K_w = 1.008 \times 10^{-14}$, and $m_s = 5.000 \times 10^{-3}$ mole kg^{-1}. These four equations could now be solved directly by the Newton-Raphson method, but they will be reduced first to three equations in three unknowns for simplicity. This can be done by solving (70) for $\{Ac^-\}$, giving

$$\{Ac^-\} = m_s - \{HAc\} \tag{77}$$

Substituting (77) into the three remaining equations (66), (67), and (74) wherever possible, yields the three equations

$$\left.\begin{aligned} K_a &= \frac{\gamma^2\{H^+\}(m_s - \{HAc\})}{\{HAc\}} \\ K_w &= \gamma^2\{H^+\}\{OH^-\} \\ \{H^+\} &= \{OH^-\} - \{HAc\} \end{aligned}\right\} \tag{78}$$

If equations (78) are then put in the form of equations (63)

$$\left.\begin{aligned} f(\{H^+\}, \{OH^-\}, \{HAc\}) &= \frac{K_a}{\gamma^2}\{HAc\} + \{H^+\}\{HAc\} - m_s\{H^+\} = 0 \\ g(\{H^+\}, \{OH^-\}, \{HAc\}) &= \gamma^2\{H^+\}\{OH^-\} - K_w = 0 \\ h(\{H^+\}, \{OH^-\}, \{HAc\}) &= \{OH^-\} - \{HAc\} - \{H^+\} = 0 \end{aligned}\right. \tag{79}$$

The necessary partial derivatives listed in equations (64) are

$$\begin{aligned} \frac{\partial f}{\partial\{H^+\}} &= \{HAc\} - m_s \\ \frac{\partial f}{\partial\{OH^-\}} &= 0 \\ \frac{\partial f}{\partial\{HAc\}} &= \frac{K_a}{\gamma^2} + \{H^+\} \\ \frac{\partial g}{\partial\{H^+\}} &= \gamma^2\{OH^-\} \\ \frac{\partial g}{\partial\{OH^-\}} &= \gamma^2\{H^+\} \\ \frac{\partial g}{\partial\{HAc\}} &= 0 \\ \frac{\partial h}{\partial\{H^+\}} &= -1 \\ \frac{\partial h}{\partial\{OH^-\}} &= 1 \\ \frac{\partial h}{\partial\{HAc\}} &= -1 \end{aligned}$$

Substituting equations (79) and the above partial derivatives into (64) yields

$$\left.\begin{aligned} (\{HAc\} - m_s)\Delta\{H^+\} + (0)\Delta\{OH^-\} + \left(\frac{K_a}{\gamma^2} + \{H^+\}\right)\Delta\{HAc\} &= \left(m_s\{H^+\} - \frac{K_a}{\gamma^2}\{HAc\} - \{H^+\}\{HAc\}\right) \\ (\gamma^2\{OH^-\})\Delta\{H^+\} + (\gamma^2\{H^+\})\Delta\{OH^-\} + (0)\Delta\{HAc\} &= (K_w - \gamma^2\{H^+\}\{OH^-\}) \\ (-1)\Delta\{H^+\} + (1)\Delta\{OH^-\} + (-1)\Delta\{HAc\} &= (\{HAc\} + \{H^+\} - \{OH^-\}) \end{aligned}\right\} \tag{80}$$

where subscripts are dropped to avoid cumbersomeness. Equations (80) then can be used to improve an approximate value of $\{H^+\}$, $\{OH^-\}$, and $\{HAc\}$ by solving (80) for corrections on these quantities. It now remains to find approximate values for $\{H^+\}$, $\{OH^-\}$, and $\{HAc\}$ so that the improvement of these values can be commenced. To find these approximations it is recalled that $\{H^+\}$ is considerably less than $\{OH^-\}$, and thus can be omitted from (74), yielding

$$m_s \simeq \{Ac^-\} + \{OH^-\} \tag{81}$$

Substituting (81) into (70) produces

$$\{OH^-\} \simeq \{HAc\} \tag{82}$$

Substituting (82) into the first equation in (78) results in

$$K_a \simeq \frac{\gamma^2\{H^+\}(m_s - \{OH^-\})}{\{OH^-\}} \tag{83}$$

Then solving (67) for $\gamma^2\{H^+\}$ and substituting into (83) gives

$$K_a \simeq \frac{K_w(m_s - \{OH^-\})}{\{OH^-\}^2} \tag{84}$$

which is easily rearranged into

$$K_a\{OH^-\}^2 + K_w\{OH^-\} - K_w m_s \simeq 0 \tag{85}$$

Using the quadratic formula

$$\{OH^-\} = \frac{-K_w \pm \sqrt{K_w^2 + 4K_aK_wm_s}}{2K_a} \tag{86}$$

and substituting $K_w = 1.008 \times 10^{-14}$, $K_a = 1.754 \times 10^{-5}$, and $m_s = 5.000 \times 10^{-3}$ mole kg^{-1}, into (86) gives, as the only positive root

$$\{OH^-\} \simeq 1.6948 \times 10^{-6} \text{ mole kg}^{-1} \tag{87}$$

$\{H^+\}$ can then be found by solving (67)

$$\{H^+\} = \frac{K_w}{\gamma^2\{OH^-\}} \tag{88}$$

and substituting in (87) and (76). This yields

$$\{H^+\} \simeq 7.0187 \times 10^{-9} \text{ mole kg}^{-1} \tag{89}$$

Finally it is necessary to find $\{HAc\}$. This is most simply done by solving the third equation in (78), which produces

$$\{HAc\} = \{OH^-\} - \{H^+\} \tag{90}$$

Substituting (87) and (89) into (90) yields

$$\{HAc\} \simeq 1.6878 \times 10^{-6} \text{ mole kg}^{-1} \tag{91}$$

Now these three approximations can be improved by substituting (87), (89), and (91) into (80). This produces the system of equations:

$$\left.\begin{aligned} (-4.99831 \times 10^{-3})\Delta\{H^+\} + (0)\Delta\{OH^-\} + (2.07059 \times 10^{-5})\Delta\{HAc\} &= 1.460 \times 10^{-11} \\ (1.43616 \times 10^{-6})\Delta\{H^+\} + (5.94758 \times 10^{-9})\Delta\{OH^-\} + (0)\Delta\{HAc\} &= 0 \\ (-1)\Delta\{H^+\} + (1)\Delta\{OH^-\} + (-1)\Delta\{HAc\} &= 0 \end{aligned}\right\} \tag{92}$$

If this system of linear equations is solved the following corrections are obtained

$$\left.\begin{aligned} \Delta\{H^+\} &= -1.457 \times 10^{-11} \text{ mole kg}^{-1} \\ \Delta\{OH^-\} &= 3.519 \times 10^{-9} \text{ mole kg}^{-1} \\ \Delta\{HAc\} &= 3.533 \times 10^{-9} \text{ mole kg}^{-1} \end{aligned}\right\} \tag{93}$$

If the values in (93) and the first approximations are used as directed in (65) the resulting improved values are:

$$\left.\begin{aligned} \{H^+\} &= (7.0187 \times 10^{-9} - 0.0146 \times 10^{-9}) \text{ mole kg}^{-1} \\ &= 7.0041 \times 10^{-9} \text{ mole kg}^{-1} \\ \{OH^-\} &= (1.6948 \times 10^{-6} + 0.0035 \times 10^{-6}) \text{ mole kg}^{-1} \\ &= 1.6983 \times 10^{-6} \text{ mole kg}^{-1} \\ \{HAc\} &= (1.6878 \times 10^{-6} + 0.0035 \times 10^{-6}) \text{ mole kg}^{-1} \\ &= 1.6903 \times 10^{-6} \text{ mole kg}^{-1} \end{aligned}\right\} \quad (94)$$

Since the corrections are all very small compared to the the first approximations, it is likely that further improvement of the second approximation is unnecessary. To find out whether further calculation is required, it is only necessary to calculate $\{Ac^-\}$ and then check the solution by substituting the values of the four unknowns into equations (66), (67), and (74). $\{Ac^-\}$ is conveniently found from (77) to be

$$\begin{aligned} \{Ac^-\} &= (5.000 \times 10^{-3} - 0.0017 \times 10^{-3}) \text{ mole kg}^{-1} \\ &= 4.9983 \times 10^{-3} \text{ mole kg}^{-1} \end{aligned} \quad (95)$$

Substituting (94) and (95) in the above mentioned equations gives

$$1.754 \times 10^{-5} \stackrel{?}{=} \frac{(0.92054)^2(7.0041 \times 10^{-9})(4.9983 \times 10^{-3})}{1.6903 \times 10^{-6}}$$
$$\doteq 1.7551 \times 10^{-5}$$
$$1.008 \times 10^{-14} \stackrel{?}{=} (0.92054)^2(7.0041 \times 10^{-9})(1.6983 \times 10^{-6})$$
$$\doteq 1.0076 \times 10^{-14}$$

and

$$5.000 \times 10^{-3} + 7.0041 \times 10^{-9} \stackrel{?}{=} 1.6983 \times 10^{-6} + 4.9983 \times 10^{-3}$$
$$5.0000 \times 10^{-3} = 5.0000 \times 10^{-3}$$

Since the solution checks satisfactorily, it can be accepted to the number of significant figures of the original data. Thus the solution is $\gamma = 0.9205$, $\{H^-\} = 7.004 \times 10^{-9}$ mole kg^{-1}, $\{OH^-\} = 1.694 \times 10^{-6}$ mole kg^{-1}, $\{HAc\} = 1.690 \times 10^{-6}$ mole kg^{-1} and $\{Ac^-\} = 4.998 \times 10^{-3}$ mole kg^{-1}.

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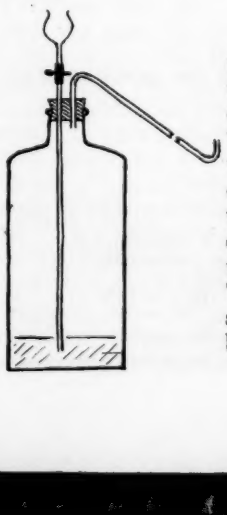
A Reagent Bottle for Dispensing Insoluble Gases

The average time available for laboratory in a high school chemistry course usually runs about fifty minutes. This allows little time for bending glass tubing and assembling equipment for the generation of oxygen, hydrogen, or other gases. As valuable as the development of these techniques may be, they take second place (in the writer's opinion) to observation of the actual chemistry involved. With this in mind, and with a budget insufficient for purchasing bottled gases, the "reagent bottle" for insoluble gases was developed.

Hydrogen or oxygen gas is collected over water in two-quart (or larger, if preferred) bottles, which are corked and stored. When a gas is needed, a bottle is fitted with the diagrammed apparatus. The delivery tube is placed in a pneumatic trough fitted with a collecting bottle. The pinch clamp is removed and another collecting bottle of water is poured through the thistle tube. The water replaces the gas, which thus can be collected in samples of predetermined volume.



Six two-quart bottles are usually sufficient for a class of twenty-five or thirty students for oxygen or hydrogen experiments. This method has two other obvious advantages: (1) it saves on chemicals and, (2) it eliminates the dangers involved when students work with hydrogen generators and with potassium chlorate. The apparatus also works well as a hydrogen source for blowing up balloons.

Proceedings of the

California Association of Chemistry Teachers

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Chemistry in Indonesia

Of the recently independent countries of southeast Asia, Indonesia is one of the most turbulent. It consists of nearly 5000 islands which formerly constituted the Dutch East Indies. Java, Sumatra, Borneo, and the Celebes are the most important, although Bali is probably best known to westerners. While there are several minorities, most of the people are of Malay descent. Although the language is of Malay origin, it has abundant words from Sanscrit, Chinese, Arabic, Dutch, and English. Nearly 90% of the 85,000,000 inhabitants are Moslem. The climate is tropical throughout.

Universities in Indonesia

The University of Indonesia has been receiving American aid for several years. This is administered by Dr. Francis Scott Smyth of the University of California. I arrived in the capital city of Djakarta in September, 1957, to teach chemistry, to demonstrate American practice in chemistry training, and to permit the Indonesian department head, Dutch-trained Dr. Lauw Soan Keng, to visit the U. S. for advanced studies. The chemistry department at the University of Indonesia in Djakarta is part of the Faculty of Medicine. There are also faculties of law, literature, economics, etc. A branch of the university for veterinary training is in Bogor, about 40 miles inland from Djakarta. The technical branch is in Bandung; its chemistry department is assisted through a contract with the University of Kentucky. There are four other major Indonesian universities: Airlangga University in Surabaya, with its branch in Malang; Gadjah Mada University in Jogjakarta; one in Bukit Tinggi, in central western Sumatra; and one in Makassar, in the southern Celebes.

In colonial times, practically all chemists in Indonesia were trained in Holland. It must take one or two decades to set up an adequate chemical education program, considering the background of scientific impoverishment of the area at the end of the revolution in 1949. Very few Indonesian-trained chemists graduate today, and those who do quickly find employment in the universities or government.

The University of Indonesia in Djakarta. The University, founded by the Dutch in the European tradition, was a hotbed of revolutionary spirit in 1945–49. With independence, administration passed entirely into Indonesian hands. Most of the officials, such as Dean Sudjono of the Medical School, are dedicated to their task and work industriously in spite of frequently discouraging circumstances.

In each of my two years of teaching general chemistry combined with qualitative and quantitative analysis, I had more than 200 medical students, and nearly 50 more in preclinical and medical technology. Most of the students were 18 to 22 years of age, and about 15% were women. I lectured in English; the students had previously studied English five or six years. The pre-university training was a year beyond that of American high schools, and included lectures in chemistry, but no laboratory work. The best pre-university students, numbering about 1300, took competitive examinations for acceptance into the Medical School. This represented a painful change from the earlier practice, in which any person could enter the first year, this privilege being considered a fruit of the revolution. Government scholarships enable quite a few students from the poorer classes to attend the university, and this is another niche in the semifeudal order of old Java. The performance of the medical students in chemistry compared favorably with their counterparts in the U. S., despite the language barrier.

Besides orienting the subject matter along more modern lines, other pedagogical changes accomplished were the correlation of lecture and laboratory work (which had formerly been more or less independent), use of new lecture demonstrations, and introduction of a weekly quiz. Much new American equipment was purchased. The physical facilities were modern, airy, and pleasant. The chemistry department was housed in an old opium factory, reconstructed for the expanded university after the revolution. The laboratory benches and furniture were made of teakwood, and there were arcaded walks between buildings. Mango trees were on each side of my lecture room. New construction goes on at a leisurely pace, employing abundant manpower and inefficient methods. Chickens and sometimes a few goats may be seen on the campus, and an endless procession of pedestrians, tradesmen, cars, carts, and trishaws can be seen on the street fronting the university.

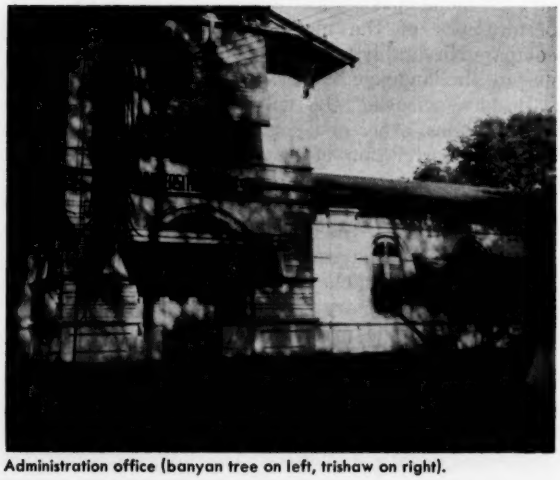
With several assistants (Messrs. Chattam, Suwandi, and Rasimin), I was able to carry out a modest piece of research on the decomposition kinetics of copper hydride. Most of the research in the university is in biochemistry or biology, and considerable notable work is being done in hematology and parasitology. For those faculty members with medical degrees, the problem of

conducting research on the low university salary versus earning extra income via medical practice is severe, and the temptation toward the latter choice is almost overwhelming.

The shortage of qualified professors is critical. We were never able to locate an Indonesian understudy who had sufficient training to fill my position permanently, but one competent lecturer, Mr. Nazir, is coming to this country for graduate work. Professor Donosupotro was flown regularly to Makassar, in the Celebes, to lecture in physics.

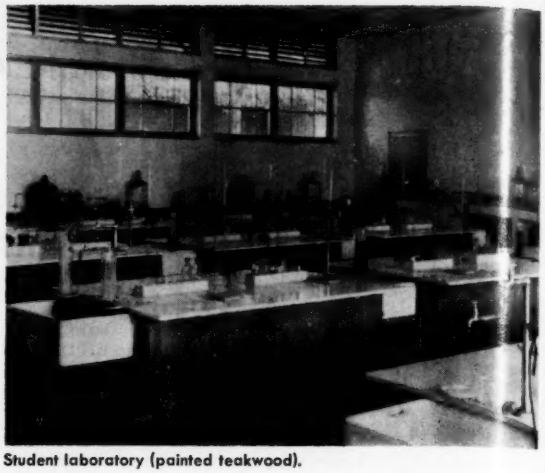
One of the best students in my class, Rustam E. Harahap, came to me at the end of the semester and announced that he must drop out because he had contracted tuberculosis. Poverty and undernourishment make Indonesians especially susceptible to this disease (nearly 5% are said to be infected), but they are experts in its treatment, by rest and chemotherapy. Within a year Mr. Harahap was back.

Perhaps the first thing which impresses an American professor in Indonesia is the exaggerated respect shown him. Students would stand and bow when I approached. Two subjects most often heard discussed among students were sputnik and Little Rock. The Communist Party is very strong in Indonesia, and some students were boldly sympathetic with it. One of the attitudes toward education most objectionable to Americans is that the goal of university work is to endow the graduate with a privileged social status. One role of Americans in this environment is to demonstrate that it is not necessarily beneath the dignity of an educated person to do a menial task, and that sharp class distinctions can be softened without bruising one's ego excessively. The lengths to which people will go for an education or at least a certificate thereof are illustrated by some veteran students in Surabaya who, feeling their chances of passing their examinations were slim, kidnapped the examining board and tried to extort assurance that they would pass.



Administration office (banyan tree on left, trishaw on right).

Occasionally on the campus, one can hear students singing in the balmy evening; some melodies are elusively familiar. The dialects are being replaced slowly by the official Indonesian language, although Dutch is still the common nonclassroom language among the intelligentsia.



Student laboratory (painted teakwood).

There is an astonishing admixture of modern Western concepts and ancient Javanese superstition to be found in Indonesia today. The belief that disease is caused by evil spirits is still prevalent, and *ducuns* (witch doctors) are employed to help the sick, sometimes successfully. Even the advanced medical students at times have difficulty in resolving their early and recent training. Once I found that some of my Bali wood carvings were infested with wood-boring beetles and decided to asphyxiate them with hydrogen cyanide. For this purpose I employed a polyethylene bag, and was assisted by Rachman, a janitor from Bantam in western Java. He sensed the respect I accorded the cyanide, and watched the bag balloon up with the deadly gas. Later he asked one of my assistants, "That Prof. Dr. Warf, is he trying to bring those carvings to life?" The question was sincere. Rachman had never gone to school and was brought up on black magic and goblins. But when an explanation was given him, he quickly understood.

The Eijkman Institute. The Dutch physician, Eijkman, recognized the origin of beriberi as a dietary deficiency (1890). Originally, the institute named for him was devoted to the study of tropical diseases. Today it also has divisions of nutrition, public health, drug control, and related fields. It has the only recording infrared spectrophotometer in Indonesia.

A Scientific Meeting

The First National Congress of Science (Konggres Ilmu Pengetahuan Nasional I) was held in August, 1958, in the mountain city of Malang in East Java. One drives through stately teakwood forests on the way, enchanted by the monkeys who scamper away from the car. Many participants stayed in a resort just outside town, near ruins of huge Dutch homes which were burned during the revolution. The ravines were filled with kapok trees, with their limbs at characteristic right angles to the trunk.

The meeting resembled our own AAAS meetings. It was thoughtfully planned and expertly conducted. The government put a lot of money into it, and President Sukarno himself gave an address. In the middle of the technical sessions, demure Javanese maidens served refreshments, consisting of a soft drink and deli-

cious, sticky rice paste cakes wrapped in banana leaves, delightfully if inappropriately called *nagasari*, which means essence of dragon. There were several hundred papers given in the physical sciences, pure mathematics, and the life and social sciences.

Natural Resources and Industry

The proven natural resources of Indonesia are vast, ranking about fifth of all countries. The mineral reserves include tin, found mostly in the islands near the Malay peninsula; petroleum, in Sumatra; iron and nickel, in the Celebes and southern Sumatra; pyrolusite, in Borneo and Java; and considerable small mines yielding diamonds and precious metals. The principal plant products for export are rubber, copra, spices, rattan, hardwood, tea, and coffee. Regrettably, only tin and oil of the mineral deposits are exploited significantly, and even here production could be expanded. Industries based on the other deposits are primitive or nonexistent.

The largest industrial enterprises in Indonesia are several petroleum refineries in Sumatra and in eastern Borneo. I visited these and observed that they were very modern and efficient. A large cement plant is in Java, near Surabaya. There are small foundries for production of copper alloys and silver, and for fabrication of these metals, mostly by laborious hand operations. A small plant for refining volcanic sulfur is found in the central Javanese mountains. A volcanic lake in eastern Java contains several per cent sulfuric and hydrochloric acids, but no use has been developed for its contents. There are some caustic soda and soap plants, and coconut oil is hydrogenated to margarine.

Of the many drugs produced, quinine is the most important. Malaria is still found in many rural areas, and the modern synthetics like chloroquin are too expensive. Batik, a fabric used in the national costume, is colored with vegetable dyes, but imported coal tar dyes are replacing the natural materials. Tannin is produced from the bark of African acacia trees grown in central Java. I visited a small plant for making citronella oil. The coarse grass is partially burned, and the products cooled; then the oil, which is heavier than water, separates from the condensate.

Arcaded walk on campus.

Certain food products deserve mention. Tea leaves are processed by an enzymatic reaction, and the fruity part of coffee beans is removed similarly by fermentation. The very best coffee, however, is prepared with the assistance of a civet-like animal, the *luak*, which climbs the trees at night, feels each bean, and selects only the ripest for its diet. The beans are excreted, and are collected under the tree each morning. There is a dehydrated soy milk factory in central Java whose product, *saridele* (from *sari*, essence, and *kedele*, soybean), is a product of Indonesian research.

I visited Ambon, the capital island of the Malucca or Spice Islands, just west of New Guinea. The principal spices are nutmeg and clove, and when the latter is in bloom, the whole grove is perfumed by the fragrance. The oils from these spices are prepared by steam distillation. A medicinal oil, *minjak kaju putih* (literally, oil of white wood), is similarly separated from the leaves of a eucalyptus-like tree. The nearby island of Seram is wild and primitive and has forests of ironwood and damar trees. The latter are tapped, and the sap which they exude is desiccated to produce a gum, used in manufacturing varnish. I also visited facilities for making sago, a starchy food from a palm. The pithy interior of the trunk is pounded into a pulp, and the slurry of sago strained from the fibrous residue.

Indonesia Today

Indonesia today is in turmoil. Inflation is a symptom and cause of deteriorating economy. A feeling for separatism by the outlying areas has already produced revolution in some parts of Sumatra and the Celebes. The Western and Sino-Soviet powers are competing to influence Indonesia, through men, machines, and books. The principal benefits of the revolution, a feeling of national independence and an intensely expanded educational system, have contributed weightily toward sufficient stability to adhere the republic together politically, at least to date. Progress has been made also in the control of disease, to considerable degree through UNESCO. Yaws has been virtually eliminated, and malaria, trachoma, tuberculosis, and leprosy are under better control than ever before. Southeast Asian countries seem uncritically to accept education as the answer to their problems, just as Americans regard "research" as a panacea. Considering the ingenuity of the people and the resources of their land, Indonesia has immense possibilities; in a rational world it might become a modern Elysian field.

✦ ✦ ✦

Report of the New England Association of Chemistry Teachers

Donald R. Moore
The Trubek Laboratories
East Rutherford, New Jersey

The Art and the Science of Perfumery

Man lives in a world of odors, some of which are pleasant and some of which are not. This has always been so; early man must have been more aware than we of the varied smells about him, for he had a much keener olfactory sense. He was naturally attracted to objects with a pleasing fragrance and valued them, so that the arts of perfumery were developed early in history. They have been a part of every civilization since. In the beginning odorants were used only in religious rites and in medicine; later they were adopted by commoners. The pagan priests used sweet-smelling saps and gums in their votive offerings; the ancient Chinese used musk in their temples; and the Egyptians buried incense and other odorants with their dead Pharoahs. Perfumes became one of the chief items of ancient trade, with myrrh and frankincense from Arabia being much prized.

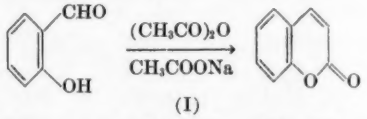
The Greeks, save only the Spartans, protected and sponsored perfumery, and the Romans used perfumes to fantastic excess. The Romans were great traders, and when trading went awry, Pliny complained of military expeditions that were designed to bring perfumes back to Rome.

In the period from the fall of Rome to the Renaissance the Arabs and the Persians improved the methods of manufacture, introducing two most important innovations. The first was the use of distillation to remove the volatile essential oils from the bark, petals, or leaves of their natural sources. The second was the introduction of ethyl alcohol as the solvent for perfume bases. Formerly olive oil had been used, but its oily character, odor, and poor efficiency as a solvent made the introduction of alcohol extremely important. Many choose to consider this event as marking the beginning of modern perfumery.

Nearly every country has some indigenous flora which are capable of producing commercial essential oils. For example, in the United States is the peppermint plant whose oil is highly prized in both flavor and odor compositions. In southern France the climate, rainfall, and soil quality combine to produce appropriate conditions for the cultivation of many of the flowers, herbs, and shrubs which are the starting materials for perfumes. The quiet region around the small town of Grasse began to be developed late in the eighteenth century and is today perhaps the most important single source of the raw products. Reunion Island, off the coast of Madagascar, is another very important center.

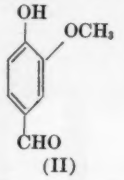
First Syntheses

Over the centuries the preparation of perfume has been an art. The alchemists were interested in these pleasantly aromatic oils, and succeeded in separating many pure substances from the multitude often present in a single oil. However, as a science, it was not until the development of organic chemistry that there were any significant developments in the chemistry of perfumery. Interestingly enough many of the early successes of organic chemistry were in the field of the aromatics. Thus in 1868, Perkin discovered the reaction which today bears his name, and the condensation of salicylaldehyde with acetic anhydride soon followed. This resulted in the first synthesis of a natural odorant, coumarin (I), which occurs in many plants and has the familiar odor of new-mown hay:



(I)

In 1876 Tiemann synthesized vanillin (II), the active flavor and odor constituent of the vanilla bean:

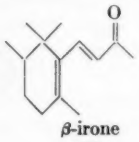


(II)

This had an interesting economic effect. Before Tiemann's synthesis, vanillin was quite expensive, and it was a common practice for dealers to store their supplies in safes overnight. The first synthetic vanillin cost $250 per pound, but as improvements have been made the price has dropped to less than $5. As a result, vanillin, one of our best odorants and flavors, may now be found in countless perfumes and candies.

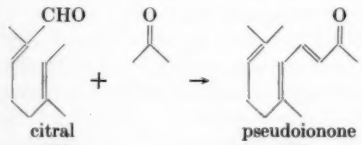
It was less than twenty years later that this same Ferdinand Tiemann became interested in the odor of the violet—an odor so prized that oil of violet sold for several thousand dollars per pound. Tiemann wished to isolate the constituent responsible for the odor and to determine its structure so that he might find an inexpensive way to produce this valuable substance artificially. However, the cost of sufficient oil of violet to permit this research was prohibitive. It takes 2000 violets to furnish 1 pound of petals, and 33,000 pounds

of petals to furnish 1 pound of the oil—hence the high price. Tiemann was familiar with orris root— the root of the iris plant, which had an odor much the same as the oil of violet, and was furthermore much cheaper. He set to work with orris root and soon isolated a ketone, which he named irone. After experimentation he arrived at a reasonable structure for the compound. Tiemann reasoned that citral (IV) and acetone should condense to give the new material, but when this was done, the result was a dismal failure. The synthetic product had a peculiar odor which did not resemble irone at all. Today we know the correct structure of irone (β-isomer, III) to be:



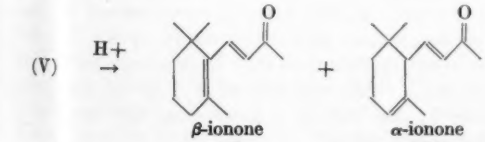
β-irone
(III)

However, Tiemann's condensation had produced a quite different compound, today called pseudoionone (V):



citral (IV) + pseudoionone (V)

With the correct formulas in hand we can see the trouble. Tiemann's empirical formula was incorrect, irone actually has one more methylene unit than his condensation product, and further the condensation product is acyclic while irone has one carbocyclic ring. Yet this was not failure but was enormous success. Exactly what happened that day in Tiemann's laboratory is not clear, but the story is told that Tiemann gave a dirty flask containing some pseudoionone to his assistant to be cleaned; the assistant poured hydrochloric acid into the flask to help clean it, and a powerful odor of violets rapidly filled the laboratory. This makes a good tale, but it is more probable in view of Tiemann's brilliant researches that the discovery arose not by mere chance, but as a result of tedious testing of his disappointing condensation product. Today we know that the acid effected a cyclization of pseudoionone to a mixture of β- and α- ionones (VI and VII.)



(V) $\xrightarrow{H+}$ β-ionone (VI) + α-ionone (VII)

which have odors quite similar to the irones. Tiemann thoroughly investigated the chemistry of the ionones and laid the groundwork for the production of a series of some of our most valuable and popular aromatics—the ionone family. These researches represented one of the first cases of the duplication of a natural aroma by man, as well as the creation of compounds unknown to nature for use as odor substitutes. Interestingly, several workers have since discovered the ionones in nature as trace components of various natural oils.

This process of isolating natural aromatic substances and duplicating their odor, either by direct synthesis or by discovering an adequate substitute, is still continuing. At present a large number of natural oils have synthetic duplicates. In many cases these provide an improvement on nature, for there is less tendency for variation from sample to sample and more uniform odor is thus possible.

Odors and the Sense of Smell

The story of the ionones leads us directly to ask some searching questions about odor. Why do β- irone and β-ionone have quite similar odors although they are different compounds? Why does pseudoionone, which is not very different from these have a vastly different odor? What is there about β-ionone that gives it the odor of violets? For that matter, what is there about β-ionone that gives it an odor of any kind?

Before considering any of the theories of odor, it will be well to collect some of the facts which are known about the subject. Although some of these observations are obvious, they must be explained by any master theory that is to be considered acceptable.

Some substances are odorous and others are not. Those with a high molecular weight usually are not. Substances with quite different chemical structures may have similar odors, and those with similar structures usually do. Exceptions are known, however, where geometrical isomerism produces a marked change. For example: *trans*-α-ionone has a violet odor, while the *cis* modification smells like cedarwood. The quality as well as the intensity of an odor may change upon dilution; indole is a familiar example. Pure indole has a potent odor which may best be described as downright disgusting. When diluted, however, this changes to the beautiful floral fragrance of jasmine.

All normal people have a sense of smell. Its loss can usually be traced to brain injury, injury to the olfactory nerve, obstructed nasal passages, or the like. There are cases of preferential anosmia, cases in which the person has lost or never had the ability to smell a particular kind of odor. They have not been very well investigated and may be more widespread than is realized. For example: there are people who cannot smell the musk odor, which is heavy and powerful—to them the substance may be completely inodorous. The sense of smell is rapidly fatigued. All chemists are familiar with the hydrogen sulfide odor in an analytical laboratory and also with the fact that once in the laboratory for a short time, the nose is fatigued to the point where the odor is no longer noticeable. If one leaves for a period, the nose may be refreshed, so that when one returns the odor is again all too discernible. Fatigue for one particular odor does not affect dissimilar odors. It should be quite possible to smell a rose even if the nose has been fatigued from hydrogen sulfide. Odors may mask other odors; the lilac or pine scents used today to mask household odors are familiar examples.

We can smell at a distance and odor travels downwind; the material producing the odor may be at quite a distance. Most animals have a stronger sense of

smell than man. In comparison with human capabilities, some forms of life seem to possess amazing powers of olfaction. One scientist tells of a trip to the country on which he trapped a newly-hatched female Emperor moth, returned to the heart of town, and placed the female in a small cage in front of his open window. Although he had never seen an Emperor moth in the city before, within a six and one-half hour period, he managed to trap 127 males attracted to his female. This and many similar instances require the conclusion that lower animals far outdistance us in olfactory power.

Theories of Odor

With these observations in mind we can return to the questions about odor. Although there has been an enormous amount of work carried out to answer questions about it, completely acceptable answers are not known. In the last century perhaps as many as twenty-five major theories of odor have been advanced. Theories abound although they may be conveniently classified for brief discussion into only two categories: first, radiation or vibration theories, and second, chemical theories.

Let us consider first some examples of the radiation-vibration theories. All of these are predicated on the idea that molecules absorb or emit radiations or vibrations which are responsible for odor. In 1916 Heyninx proposed that molecules absorb ultraviolet light and that our noses sense odor from differential absorption by the odorant. However it may be pointed out that molecules which have quite similar ultraviolet spectra may have quite different odors; hydrogen cyanide and water have quite similar absorption spectra, but hydrogen cyanide smells like bitter almonds and water is odorless. In 1922 Ungerer and Stoddard suggested that the odorant molecules are vibrating and that intermolecular vibrations affect the olfactory nerves. Each molecule would have a definite characteristic vibration which is too slight to be detected by any instruments. A major objection to this theory arises from the vast bulk of knowledge that points to a correlation between chemical reactivity and odor. It is difficult to reconcile this with such a theory. In 1937 Dyson proposed that three requirements are essential for odor: volatility, solubility in the fatty tissues of the nose, and a shift in the Raman spectrum of the odorant. One may certainly agree with the essential character of the first two requirements, but there is no universal agreement that a Raman shift is responsible for odor, even though it may be true that all odorous molecules do display a shift. Conclusive evidence is unfortunately lacking.

Chemical theories of odor rest on an unspecified chemical reaction as crucial in olfaction. The fact that unsaturation is extremely important in enhancing odor was early recognized. Three theories, that of Woker in 1906, Marchand in 1915, and Delange in 1922, held that unsaturation was the cause of odor. Naturally these theories find it difficult to explain the odors of saturated compounds. In 1920 Ruzicka, who has been concerned with the chemistry of odorous substance for a half century, advanced the theory that functional groups (hydroxyl, etc.) of the odorant (designated osmophores) reacted chemically with the odor receptors in the nose (osmoceptors). This is undoubtedly part of the answer but is still too indefinite to permit reliable predictions.

In spite of the lack of a truly comprehensive theory of odor, some of the principles upon which the ultimate theory must be based may be listed:

The substance, if it is to be odorous, must have a certain volatility so that molecules of it can reach the olfactory membranes. There is evidence that not much volatility may be needed, since for the more powerful odors—muscone, for example—a calculation will show that as few as 100 million molecules will suffice.

There is rather general agreement that fat solubility is essential, and that some water solubility may be desirable for the substance to participate in the odor process.

The chemical reactivity is very important, and molecules which are very reactive are likely to have strong odors. Unsaturation usually intensifies the odor. The odor process may include the reaction of the molecules with an enzyme, the formation of weak addition compounds, or the establishment of hydrogen bonds. Perhaps a number of such reactions will be required.

Molecular vibrations may play a role; for theories based on them have found great success in explaining the fact that two odorous materials when smelled together may be odorless. Cancellation of odor may be visualized much as one pictures two waves of water so oriented that their effects cancel one another.

Any comprehensive theory must consider the strong possibility that several processes, both chemical and physical may occur simultaneously.

Uses of Odorants Increasing

Thus we cannot yet say why irone smells like a violet and not like a rose. Much research has been done, but too many questions are still unanswered. At an odor conference devoted to just these very problems, Beets recently stated, "One conclusion, however, is obvious. Up to this moment, not a single concentrated effort has been undertaken in order to solve the problem of odor." The challenge remains, but in spite of the lack of a comprehensive odor theory, how perfumery has grown! Applications are commonplace now that could not even be imagined twenty years ago. Odorants today repel sharks and sell automobile tires. Chemists have isolated the potent odor of a dead shark and synthesized the compound responsible. Dispersal of this material in the water around downed airplanes has repelled sharks and saved many lives. Synthetic rubber in automobile tires may have an unpleasant odor if untreated. The addition of a little of the proper perfume to the rubber composition can remove the customer's opposition.

An interesting story is told of the hosiery manufacturer who conducted a survey in which one of two identical pairs of women's stockings was lightly perfumed, and the two pair then presented to a group of women who were asked to give a preference and their reasons. The women overwhelmingly chose the lightly scented hose, and gave among their reasons: "obviously better quality," " has a better feel to it," "don't know why, I just like it better." Not one of the women was

apparently aware that one pair smelled different. Similar experiments have been carried out with men's artificial leather wallets—one lightly perfumed, the other not—with much the same overwhelming preference for the treated one.

Applications for odors are growing at a rapid rate and with them the perfume industry. We do indeed live in a world of odors, and if perfumery makes our world of odors safer and more pleasant, it should make our living in it more enjoyable.

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SAGARIN, E., "The Science and Art of Perfumery," McGraw-Hill Book Company, Inc., New York, 1945.

Presented at the 21st Summer Conference of the New England Association of Chemistry Teachers, University of Connecticut, Storrs, Conn.

Chem Ed

LETTERS

To the Editor:

In the March, 1960, issue of the JOURNAL OF CHEMICAL EDUCATION, I read with interest the Letter to the Editor by Crayton M. Crawford, Mississippi State University, concerning the washing of laboratory glassware.

In my experience of over 25 years of supplying glassware to laboratories, I have found that glassware is abused by the various processes of washing. The simplest method of washing glassware under most conditions is to prepare the utensils as follows:

Rinse and place in water fully covering the glassware and allow to stand until ready for washing.

About 2 to 3 hours before washing, add a mild detergent, and allow to soak to remove any grit and foreign matter.

Wash either by hand with a brush or in a mechanical washer.

Rinse thoroughly with clear water—preferably distilled water.

Allow to dry in a warm cabinet.

This method should leave most glassware in perfect condition for use.

WILLIAM LEBOWITZ

STANDARD SCIENTIFIC SUPPLY CORP.
808 BROADWAY, NEW YORK 3, N.Y.

To the Editor:

In his article, "Estimating Standard Oxidation Potentials" (March, 1960, p. 147) Csányi performs a valuable service in giving a simple graphical interpretation to the Luther-Wilson rule. As Csányi correctly states, from two measured electrode potentials

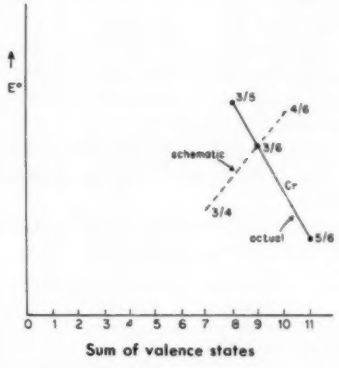
$$M^{a+} = M^{b+} + (b - a)e^- \quad \ldots \quad \ldots \quad E^\circ_{a/b}$$
$$M^{b+} = M^{c+} + (c - b)e^- \quad \ldots \quad \ldots \quad E^\circ_{b/c}$$

one can obtain the unmeasured potential $E^\circ_{a/c}$ from the fact that

$$\frac{E^\circ_{b/c} - E^\circ_{a/b}}{E^\circ_{a/c} - E^\circ_{a/b}} = \frac{(b + c) - (a + b)}{(a + c) - (a + b)} \quad \ldots \quad \ldots \quad (1)$$

This means that if, on a graph, the coordinates of two points are $E^\circ_{a/b}$, $(a + b)$ and $E^\circ_{b/c}$, $(b + c)$ then $E^\circ_{a/c}$ is found where the line joining the two points cuts $(a + c)$. This is a useful and simple check on the self-consistency of the three potentials.

However, Csányi states that further unknown potentials $E^\circ_{i/j}$ involving the species M can be estimated by finding where $(i + j)$ cuts the line given by equation (1). This is not a valid procedure, and indeed it would be surprising if it were so since it could yield thermodynamic data for species which were not experimentally obtainable.



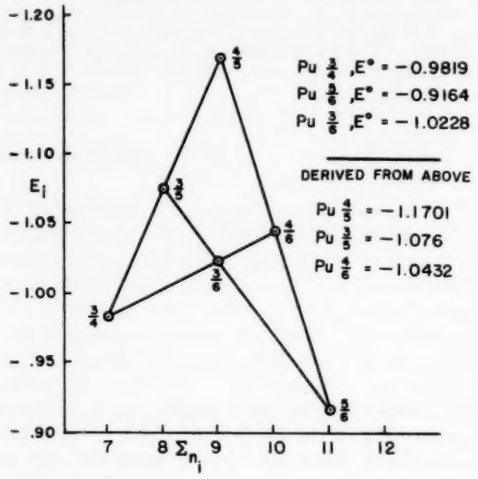
Csányi assumes that $E^\circ_{3/4}$ and $E^\circ_{4/6}$ for M = Cr necessarily lie on the straight line joining $E^\circ_{5/6}$, $E^\circ_{3/6}$, and $E^\circ_{3/5}$; this cannot be inferred from equations of type (1) which tell us nothing concerning the slope or intercept of the straight line in question. Hence, in general, the points $E^\circ_{4/6}$, $E^\circ_{3/6}$, and $E^\circ_{3/4}$ lie on a different straight line from that on which $E^\circ_{5/6}$, $E^\circ_{3/6}$, and $E^\circ_{3/5}$ lie. (See figure.)

In short, the method proposed by Csányi can be used to estimate a potential $E^\circ_{a/c}$ from two potential measurements of type $E^\circ_{a/b}$ and $E^\circ_{b/c}$ but cannot be used to deduce any further potentials.

H. F. HALLIWELL

UNIVERSITY COLLEGE OF NORTH STAFFORDSHIRE
KEELE, STAFFORDSHIRE, ENGLAND

EDITOR'S NOTE. A communication from Dr. J. S. COLEMAN and Dr. R. A. PENNEMAN of the Los Alamos Scientific Laboratory has just been received which makes the same analysis as does Professor Halliwell (the misleading extension of a valid thermodynamic rule in cases where it is not valid). To further illustrate the fact that series of related E°'s fall on lines which *intersect* rather than have a common slope they supply a graph which strikingly demonstrates the relationship between the potentials of the plutonium oxidation states.



To the Editor:

In the March, 1960, issue of the JOURNAL OF CHEMICAL EDUCATION you have described an experiment under "Tested Demonstration" that is potentially very dangerous. The experiment is "Burning without Access to Air."

I performed this experiment in college in 1946 with rather unpleasant results. The test tube exploded after addition of $KMnO_4$ crystals. It took weeks for some glass particles to come out of my hand and face, and it was only the fact that I had glasses on and that I dunked my head into a sink full of water that saved me from serious acid burns.

I later learned that the explosion was probably caused by the formation of highly unstable permanganeous acid.

The warning of possibility of an explosion should accompany this demonstration.

VINCENT VODICKA

GENERAL ELECTRIC COMPANY
CLEVELAND 12, OHIO

To the Editor:

The article by H. B. Thompson on projector displays of atomic and molecular orbitals (J. CHEM. EDUC., **37,** 118 (1960)) is an excellent suggestion to those of us who like to introduce modern electron theory in the elementary courses. Two inadvertencies need to be corrected, however.

First, the equations for the ψ's contain small errors. I believe that Thompson intended $\psi = 0.56\ e^{-r}$ for the 1*s* orbital of hydrogen rather than $0.32e^{-r}$ (i.e., $\pi^{-1/2}$ rather than π^{-1}). Also, wave functions for carbon 2*s* and 2*p* electrons are of the following forms, where *a* and *b* are constants:

$$\psi_{2s} = a(2 - br)e^{-br/2}$$

$$\psi_{2p} = a(br \cos \phi)e^{-br/2}$$

which are somewhat more complicated than indicated in the article.

Second, the pattern for the 2*s* orbital (Figures 1 and 4) should not have a node but rather a maximum at the center (as for all *s* orbitals). The 2*s* node is a spherical surface which for carbon is about 0.6 Bohr radii from the center. A pattern for this orbital can be approximated by setting up six concentric circles of relative radii 1, 3, 5, 7, 11, and 15, and assigning the following relative densities to the center and the annular rings (from the center outward): 5, 2, 0, −1, −2, and −1. The negative sign means in Thompson's method a rotation of the anisotropic material. Use of this 2*s* gives a much improved *sp* hybrid. (The 2*p* pattern by Thompson is an excellent presentation.)

A series of photographic representations which would be of considerable help in setting up further patterns by Thompson's method may be found in "Principles of Modern Physics," by R. B. Leighton (McGraw-Hill, N. Y., **1959,** pp. 178–9). A complete set of normalized wave functions for $n = 1, 2$, and 3 is given in "Quantum Chemistry," by H. Eyring, J. Walter, and G. E. Kimball (Wiley, N. Y., **1944**) on pp. 89–90. There does not seem to be available any complete set of contour drawings.

IRWIN COHEN

YOUNGSTOWN UNIVERSITY
YOUNGSTOWN 2, OHIO

To the Editor:

Dr. Cohen is correct in asserting that my wave functions are in need of correction. These should read:

$$\psi_{1s} = 0.56\ e^{-r}$$

$$\psi_{2s} = 1.1\ re^{-1.625r}$$

$$\psi_{2p} = 1.9\ xe^{-1.625r}$$

where r is a radial coordinate while x is a cartesian coordinate. Dr. Cohen's statement that the 2*s* orbital should not have a central node is correct for hydrogenlike orbitals but not for Slater's approximations as specified in my article. The functions used are chosen to approximate an orbital formed under interactions with the other electrons in a carbon atom. A discussion of these functions is given by Eyring, Walter, and Kimball on pp. 162–3, or in "Valence," by C. A. Coulson (Oxford University Press, **1952,** pp. 40–41.)

Perhaps hydrogenlike orbitals would be better from the instructional point of view, since these introduce fewer ideas to be explained at one time to interested students.

A more serious error from the point of view of the person choosing to construct a set of models occurs in the legend to Figure 4. The scale given should read (× 1/3). We have available full-scale templates for these orbitals and certain others which we will send to anyone interested on request.

H. BRADFORD THOMPSON

GUSTAVUS ADOLPHUS COLLEGE
ST. PETER, MINNESOTA

Chem Ed

BOOK REVIEWS

Chemical Analysis

Herbert A. Laitinen, University of Illinois, Urbana. McGraw-Hill Book Co., Inc., New York, 1960. xiv + 611 pp. Figs. and tables. 16 × 23.5 cm. $12.50.

In the preface the author states that "This book is intended primarily to serve as a textbook at the advanced undergraduate and beginning graduate level for courses stressing the fundamental principles of analytical chemistry. In addition, it is hoped that it will serve as a reference work and guide to the literature for instructors in quantitative analysis and for practicing analytical chemists."

Without question, the author has done his part in distinguished fashion. It is to be hoped that those for whom the book is intended soon find a place for it, not on the book shelf but on the desk.

With the stress now placed on instrumental methods, it is refreshing to find a work of this calibre centered around the fundamental principles underlying chemical methods of analysis. The book wisely makes no attempt to include detailed descriptions of analytical procedures. The analyst seeking a proven method for the determination of germanium in coal ash, for example, will be forced to look elsewhere. But for one interested in the fundamentals, this book will serve as an admirable guide.

A mere listing of the principal topics covered in its 27 chapters fails to provide an adequate idea of the breadth and depth of the coverage. Acid-base equilibria in water and in non-aqueous solvents is followed by a discussion of the application of these principles. Six chapters are devoted to the precipitation process, properties of precipitates, etc. Complex formation and precipitation titrations are covered in two chapters. The chapter on organic reagents also includes material on extraction equilibria. A discussion of electrode potentials is followed by consideration of electrolytic separations. Oxidation-reduction titrations are discussed before separate chapters devoted to the more common (and some less familiar) oxidants and reductants. A separate chapter considers the topic of reaction rates, another treats that of multistage separation methods, while the important topics of statistics and sampling are accorded thorough and thoughtful treatment in the concluding two chapters. It should be emphasized that the discussion of all of these subjects is at an advanced level.

The use of the work as a textbook is greatly strengthened by the inclusion of numerical problems. The book contains 133 problems for student exercise plus 82 examples which are solved in the text. Answers are given in most cases. The problems are good and appear to represent real situations.

The book is well documented, and literature references are found as footnotes on each page—a great convenience in a work which will be used as a reference. The book appears to be remarkably free from the errors and inconsistencies which so often plague a new work of this magnitude.

In summary, this book is recommended with enthusiasm. It should be a part of the library of every graduate student with an interest in analytical chemistry. Perhaps even more important will be its perusal by those teaching quantitative chemistry, for assuredly the careful reader will find many topics discussed which can be introduced, albeit briefly, even at the elementary undergraduate level. The significance of reaction mechanisms of the common redox reactions and the importance of reaction rates are but two such examples.

The author is to be congratulated on a fine achievement.

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The Proton in Chemistry

R. P. Bell, Oxford University. Cornell University Press, Ithaca, New York, 1959. vii + 223 pp. Figs. and tables. 16 × 24 cm. $4.75.

A great deal of research has been done on proton-transfer processes since the publication in 1941, of "Acid-Base Catalysis." Bell's new book, which has been eagerly awaited, does an excellent job of presenting the recent developments in the field. The chapter on relaxation methods for measuring proton-transfer rates and the illuminating chapter on the non-classical behavior of hydrogen isotopes are particularly timely. Other topics brought up to date are the H_0 function and concerted versus consecutive reaction mechanisms.

The problem of the relation between structure or solvent and reactivity is treated not only in a chapter on thermodynamic functions relating to acid-base equilibria but also elsewhere in the book. Our present ability to deal with this problem theoretically is in a highly unsatisfactory state, not merely with regard to proton transfer reactions but for reactions in general. The trouble is that our theories based on first principles are strictly applicable only to gaseous systems at absolute zero, while most authors (unlike Bell) are unable to resist the temptation to apply these theories in a naive way to reactions in solution near room temperature. Aside from necessity, which sometimes spawns things considerably less desirable than invention, there are some rather feeble arguments for hoping that the absolute-zero-gas-phase theories might be applicable to the free energy quantities observed under the usual conditions. Although Bell repeats these arguments (pp. 70–73), he is on the whole careful to warn his readers against excessively naive or dangerously optimistic applications of theory. For example, on pages 64–66 he points out that the $T\Delta S^0$ contribution to the relative strength of an acid can be of equal magnitude to the ΔH^0 contribution. On page 69 he writes: "There is obviously no particular virtue in the standard temperature 25°C, and

Reviewed in This Issue

Herbert A. Laitinen, Chemical Analysis
R. P. Bell, The Proton in Chemistry
Max Tishler, Editor-in-Chief, Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Volume 39
W. G. deJong, General Crystallography: A Brief Compendium
E. J. Williams, Regression Analysis
Corwin Hansch and *George Helmkamp*, Organic Chemistry: An Outline, Problems and Answers
Frederick A. Gibbs, Editor, Molecules and Mental Health
J. D. Waldron, Editor, Advances in Mass Spectrometry
F. Albert Cotton, Editor, Progress in Inorganic Chemistry. Volume 1
Richard E. Brink, Donald C. Gipple, and *Harold Hughesdon*, An Outline of United States Patent Law
Emilio Segre, Leonard I. Schiff, Gerhart Friedlander and *Walter E. Meyerhof*, Editors, Annual Review of Nuclear Science. Volume 9
D. Hadzi, Editor with H. W. Thompson, Hydrogen Bonding
R. M. C. Dawson, Daphne C. Elliott, W. H. Elliott and *K. M. Jones*, Editors, Data for Biochemical Research

it is therefore dangerous to give structural interpretations of small differences in dissociation constants at this temperature, as has often been done." He also points out that structural effects will not necessarily be independent of solvent—even qualitatively—and that the continuum model will not always take adequate account of solvent effects. Thus on page 92 he writes: "...but it appears little more than a coincidence that the other three acids [HCl, HBr, and HI] preserve the same order [of strengths] in solution as in the gas phase. This is one of many instances in which dissociation constants in water appear to reflect molecular regularities more faithfully than might be anticipated." On page 67 he cites some drastic conflicts between theory and experiment and writes: "... the use of the dielectric constant is a crude macroscopic method of allowing for the orientation of the solvent molecules in the field of the ion, and there is no doubt that it is necessary to take a much more specific picture of the molecular interactions involved."

Anyone doing research in the field of proton transfer reactions or in physical organic chemistry in general will want a copy of this book. It should also be valuable as a supplementary reading assignment for graduate students or advanced undergraduates.

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Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Volume 39

Max Tishler, Editor-in-Chief. John Wiley & Sons, Inc., New York, 1959. vii + 114 pp. 15.5 × 23.5 cm. $4.

In this newest volume in the noted series, 39 contributors plus members of the Editorial Board treat 28 new syntheses. This 39th release again contains the common names, the *Chemical Abstracts* names if different, the equations, procedures, notes, and additional methods of preparation. Each set of directions has been checked by members of the advisory board and associates. These tested preparations serve as a reliable source of detailed, practical directions for valuable intermediates and as models for related reactions. A recent new feature in this series is the inclusion of a statement of the merits of each preparation, indicating a synthetic method of considerable scope, a specific compound of unusual interest, a method that gives a better yield or is less laborious than other methods, etc. It is also stimulating to note that special toxic or hazardous conditions are noted with "Cautions," in italics. The cumulative subject index lists all materials contained in Volumes 30 to 39 inclusive. A detailed set of directions for future contributors is included. The style, size, appearance, and quality are identical to those of previous volumes of the series.

"Organic Syntheses" is now an American tradition and too well known and extensively used to require any elaborate description in this review. However, it appears that more care has gone into the evaluation of each entry of this volume than perhaps in some former releases. Practicing organic chemists will find the 28 preparations helpful for direct use, or as models for related reactions. Undergraduate and graduate students will gain much valuable experience and information by repeating the directions. Most libraries will continue to buy the small annual volumes. This provides ready access to the latest published directions, and greater availability by the use of small volumes to patrons. However, many practicing chemists will prefer the more compact collective volumes. This arrangement saves on cost, shelf space, and adds to general convenience. It is now time for "Collective Volume IV."

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General Crystallography: A Brief Compendium

W. G. deJong, Technical University of Delft, with the collaboration of *J. Bowman*. W. H. Freeman and Company, Inc., San Francisco, 1959. ix + 281 pp. Figs. and tables. 14 × 21 cm. $6.

The subtitle is a true characterization; this business-like little book is indeed a compendium, whose brevity is achieved by a sometimes painful terseness, and by frequent use of the shorthand of higher mathematics. It is profusely illustrated by excellent line drawings, those of projections and of crystal structures being particularly well done (by C. van Werkhoven).

The four sections of the work are entitled Geometric, Structural, Chemical and Physical Crystallography, of which the first is the largest (92 pp.) and probably the most difficult for the average chemist. It is unfortunate that geometric (morphological) crystallography and optical crystallography, which are so useful to the geologist, are not better understood and therefore more widely used by chemists. One of the reasons is certainly the large vocabulary required. The Babel tower of science is rapidly becoming a group of isolated spires built of specialized vocabularies. This book is of little help here, for its brevity precludes the subtle repetitiousness of definitions, characteristic of a good textbook, which is so helpful to the inexpert reader (who may be expected to forget the distinction between *merohedral* and *tetartohedral* by the time he gets to page 22).

The first part contains a surprisingly complete account of crystallographic calculations, projections, and descriptions, which is much more than a summary despite the fact that it is only a fraction of the length of the usual treatment. The classification of symmetry has been rewritten to conform to international terminology.

The section on structural crystallography includes an interesting historical introduction, a quite rigorous account of the diffraction of X-rays by crystals, including intensity of the diffracted ray, and a description of the various X-ray techniques for the determination of structures. (Scintillation detectors are not mentioned.)

The third part, on chemical crystallography, is disappointing in that the treatment of chemical bonding is not up to date. The metallic bond is dismissed in a few lines and there is no mention of the bond theories of Pauling, although his radius ratio effect and coordination rules are given elsewhere, strangely without reference to his famous book. Table 13 gives atomic and ionic radii, some of which differ considerably from those in familiar tables (e.g., Pauling, Zachariasen, Wyckoff). No sources are given for this table, and Zachariasen is not referred to except in a different connection. The footnote references throughout the book are numerous, but incline to older and (in the U.S.A.) obscure works. The effect of coordination number on effective radius is mentioned in one sentence. There is a particularly good drawing showing the relation of the ccp unit cell to the stacking of spheres (Fig. 106). Solid solutions are covered in a short paragraph in which palladium hydride is wrongly included and assigned an incorrect structure (*cf.* Worsham 1957).

The final part on physical crystallography requires a background of vector and tensor algebra. It covers deformations, electrical, optical and thermal properties, and hardness. The explanation of F-centers is questionable (p. 247), but otherwise this part is a good introduction into a number of most involved topics.

One doubts that, for chemists at least, this book "will serve undergraduate students as a summary of the modern view of crystallography." It is, however, an inexpensive mine of information which bridges the gap between elementary works and the several larger compendia.

The format is good, the translation excellent (with only three or four slight lapses, e.g., P. Debije, benzochinone). Only two minor typographical errors were noted (pp. 7, 227).

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Regression Analysis

E. J. Williams. John Wiley & Sons, Inc., 1959. ix + 214 pp. Figs. and tables. 15.5 × 23.5 cm. $7.50.

Three quarters of a century ago Sir Francis Galton studied the relationship between the heights of fathers and their sons. He found that although fathers of extreme height tended to have sons of similar height, the sons' heights were generally less extreme. Sir Francis described this by saying that the heights of the sons regressed, or went back, toward the average. The term "regression" has since been used to describe the statistical analysis of empirical relationships like this.

(*Continued on page A486*)